PB80-193204

A New Correlation of NH3, CO2, and H2S Volatility Data from Aqueous Sour Water Systems

American Petroleum Inst.
Washington, DC

Prepared for

Robert S. Kerr Environmental Research Lab.
Ada, OK

Apr 80

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-80-067	2.	3. RECIPIENT'S ACCESSION NO. PB 80 193204
4. TITLE AND SUBTITLE A New Correlation of NH_3, CO_2, and H_2S Volatility Data from Aqueous Sour Water Systems		5. REPORT DATE April 1980 issuing date 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Grant M. Wilson: Brigham Young University		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS American Petroleum Institute 2101 L Street Northwest Washington, DC 20037		10. PROGRAM ELEMENT NO. C33B1B 11. CONTRACT/GRANT NO. R804364010
12. SPONSORING AGENCY NAME AND ADDRESS Robert S. Kerr Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Ada, Oklahoma 74820		13. TYPE OF REPORT AND PERIOD COVERED Final 1976-1977 14. SPONSORING AGENCY CODE EPA/600/15

15. SUPPLEMENTARY NOTES
American Petroleum Institute project officer: Ron Gantz

16. ABSTRACT

A new correlation model has been developed for calculating sour water equilibrium data at temperatures from 20°C to 140°C. The correlating equations in this new sour water equilibrium model have been used to obtain a computer program capable of handling various chemical and physical equilibria of NH_3, CO_2, and H_2S in sour water systems including the effects of carboxylic acids on ammonia fixation and release by caustic addition. A bibliography of related literature data is included in the report.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ammonia Hydrogen sulfide Carbon dioxide Volatility Aqueous systems Carboxylic acids Caustic	Henry's Constants Chemical equilibrium constants	Sour water equilibria Sour water stripping Correlation of volatility data Computer program Ammonia fixation	

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

U.S. GOVERNMENT PRINTING OFFICE 1980-657-146/5655

United States
Environmental Protection
Agency

Robert S. Kerr Environmental Research
Laboratory
Ada OK 74820

EPA-600/2-80-067
April 1980

Research and Development

PB80-193204

EPA

A New Correlation of NH_3, CO_2, and H_2S Volatility Data from Aqueous Sour Water Systems

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/2-80-067
April 1980

A NEW CORRELATION OF NH_3, CO_2, AND H_2S VOLATILITY DATA FROM AQUEOUS SOUR WATER SYSTEMS

by

Grant M. Wilson
Thermochemical Institute
and Chemical Engineering Department
Brigham Young University
Provo, Utah 84602

EPA Grant no. R804364010

Project Officer

Fred M. Pfeffer
Source Management Branch
Robert S. Kerr Environmental Research Laboratory
Ada, Oklahoma 74820

Sponsored by the
American Petroleum Institute
Committee on Refinery Environmental Control

ROBERT S. KERR ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ADA, OKLAHOMA 74820

DISCLAIMER

This report has been reviewed by the Robert S. Kerr Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in ground water; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control, or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

The use of inplant processes to remove undesirable components of a wastewater stream prior to discharge to a wastewater treatment plant can often effect significant improvements in treatment plant effluent quality. This report contains the findings of a study to utilize new correlations between sour water constituents so as to improve the ammonia removal efficiency of sour water scrubbers in petroleum refineries.

William C. Galegar

W. C. Galegar
Director
Robert S. Kerr Environmental Research Laboratory

ABSTRACT

A new correlation model has been developed for calculating sour water equilibrium data at temperatures from 20°C to 140°C. The correlating equations in this new sour water equilibrium model (SWEQ) have been used to obtain a computer program capable of handling the various chemical and physical equilibria of NH_3, CO_2, and H_2S in sour water systems including the effects of carboxylic acids on ammonia (NH_3), Carbon Dioxide (CO_2), and Hydrogen Sulfide (H_2S) in sour water systems including the effects of carboxylic acids on ammonia fixation and release by caustic addition.

This new SWEQ correlation model has been used to evaluate published and new vapor-liquid equilibrium data, and comparisons are made with the Van Krevelen prediction equations as published by Van Krevelen. Average errors between calculated and measured partial pressure data can be summarized.

Both models predict low temperature data quite well, but at high temperatures the Van Krevelen model deviates considerably from measured data, and errors between the SWEQ model and measured data increase from about 11% to about 29%. Comparisons with variations of the Van Krevelen model as published by other authors have not been made.

The basic NH_3-H_2S-H_2O equilibrium program has been inserted into a tray by tray program by CONOCO. Two brief example problems have been run to date. The calculated stream requirements appear to be approximately 30 percent greater for a refluxed tower and 20 percent more for a non-refluxed unit compared to Van Krevelen - Beychok procedures. Definite conclusions cannot be drawn until wider user experience is obtained.

Details of the SWEQ correlation model, correlating equations, the computer program, and evaluations of experimental data are given in this report. This report covers a period from March 15, 1976, to March 17, 1977, and work was completed as of November 30, 1977.

CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables vii
Abbreviations and Symbols . . . . . .

1. Introduction 1
2. Project Objectives 2
3. The SWEQ Model 3
4. Computer Program Based on the SWEQ Model 20
5. Sample Problem Using the SWEQ Model 51
6. Comparisons and Evaluations Between Calculated and Measured Data 59
   Evaluation of Van Krevelen Model 59
   Evaluation of SWEQ Model 75
   Evaluation of New BYU Data 85
   Ammonia Fixation by Acids and Release by Caustic Addition 86
7. Accuracy of Correlation 91
8. Summary 92

References 94
Appendix 97

FIGURES

Number		Page
1	Sample plot of the volatility of NH_3, CO_2, and H_2S versus pH determined by caustic addition	19
2	Flow diagram of SWEQ main program	23
3	Flow diagram of option 1 of SWEQ computer program	24
4	Flow diagram of option 2 of SWEQ computer program	25
5	Flow diagram of option 3 of SWEQ computer program	26
6	Ammonia mean ratio of measured over calculated partial pressures based on SWEQ correlation	79
7	Carbon dioxide mean ratio of measured over calculated partial pressures based on SWEQ correlation	80
8	Hydrogen sulfide mean ratio of measured over calculated partial pressure based on SWEQ correlation	81
9	Ammonia mean ratio of measured over calculated partial pressures based on Van Krevelen correlation	82
10	Carbon dioxide mean ratio of measured over calculated partial pressures based on Van Krevelen correlation	83
11	Hydrogen sulfide mean ratio of measured over calculated partial pressures based on Van Krevelen correlation	84
12	Free ammonia versus pH adjustment by caustic addition at 25°C	87
13	Free ammonia versus pH adjustment by caustic addition at 80°C	88
14	Sample plot of pH versus caustic addition showing variation of pH at 25°C and at column temperature	90

TABLES

Number		Page
1	Summary of Equations Used to Calculate Temperature and Composition Effects on Henry's Law Relations[a]	6
2	Summary of Chemical Equilibria Involved in Calculating NH_3-CO_2-H_2S-H_2O Vapor-liquid Equilibria	12
3	Effect of Composition and Ionic Strength on Chemical Equilibrium Constants[a]	14
4	Summary of Temperature Parameters, Used to Calculate Chemical Equilibrium Constants in Table 1	17
5	Computer Program Based on-the SWEQ Model	27
6	Subroutine KREAC	32
7	Subroutine HENRY	33
8	Subroutine YFX	33
9	Subroutine CFX	34
10	Subroutine PHST	34
11	Subroutine SPECV	35
12	Subroutine NPH	37
13	Subroutine SPECL	38
14	Subroutine PRESY	39
15	Subroutine NTEMP	39
16	Input data for Sample Problem with SWEQ Computer Program	48
17	Computer Output from Data in Table 16 with Computer Program Based on the SWEQ Model	50

Number		Page
18	H_2S-H_2O, NH_3-H_2S-H_2O, and NH_3-H_2O Systems, Comparison of Calculated and Measured Data of Miles and Wilson[21] and of Clifford and Hunter[17]	60
19	NH_3-H_2S-H_2O System, Comparison of Calculated and Measured Data of Terres[29]	61
20	NH_3-H_2S-H_2O System, Comparison of Calculated and Measured Data of Van Krevelen, et al.[1]	62
21	H_2S in Aqueous Buffer Solutions, Comparison of Calculated and Measured Data of Shih, et al.[26]	63
22	NH_3-CO_2-H_2O and CO_2-H_2O System, Comparison of Calculated and Measured Data of Van Krevelen, et al.[1] and Data From Lange's Handbook[20]	64
23	NH_3-CO_2-H_2O System, Comparison of Calculated and Measured Data of Otsaka, et al.[22]	65
24	NH_3-CO_2-H_2S-H_2O System, Comparison of Calculated and Measured Data of Cardon and Wilson[5]	66
25	NH_3-CO_2-H_2S-H_2O System, Comparison of Calculated and Measured Data of Badger and Silver[15]	67
26	NH_3-H_2O System, Comparison of Calculated and Measured Data of Breitenbach and Perman[16,23]	68
27	NH_3-CO_2-H_2S-H_2O System, Comparison of Calculated and Measured Data of Van Krevelen, et al.[1]	69
28	Summary of References of Experimental Data	70
29	Summary of Deviation Errors Between Calculated and Measured Ammonia Partial Pressures	72
30	Summary of Deviation Errors Between Calculated and Measured Carbon Dioxide Partial Pressures	73
31	Summary of Deviation Errors Between Calculated and Measured Hydrogen Sulfide Partial Pressures	74
A1	Computer Program Used for Calculating Vapor-Liquid Equilibrium Data From the Van Krevelen Correlation . .	99

SECTION 1

INTRODUCTION

Previous design calculations of vapor-liquid equilibrium compositions in sour water strippers have primarily been based on a correlation by Van Krevelen (1) as outlined in Aqueous Wastes from Petroleum and Petrochemical Plants by M.R. Beychok (2). The Van Krevelen correlation has proved sufficiently reliable and many sour water strippers have been designed and built using his correlation as a basis. New vapor-liquid equilibrium measurements have been made since Van Krevelen's correlation published in 1949 including new measurements at Brigham Young University sponsored by the API Technical Data Committee. Although used considerably, the Van Krevelen correlation has been previously recognized to be deficient in the following areas:

1. Only data to 60°C were correlated; thus the use of the correlation at sour-water stripper temperatures of 100 to 120°C represented an extrapolation of existing data.

2. The calculation method outlined by Van Krevelen did not allow for mixtures containing ammonia over hydrogen sulfide ratios less than 1.5 in the liquid phase.

3. The calculation did not take into account reduced volatilities of hydrogen sulfide and ammonia at low parts per million concentrations due to the ionization constants of the two compounds in water.

Subsequent sections of this report give details of a new sour water equilibrium model (SWEQ) which is based on new higher temperature data and which avoids deficiencies mentioned above. This new correlation model also permits the addition of caustic for release of NH_3 held by carboxylic acids or stronger acids.

SECTION 2

PROJECT OBJECTIVES

The development of a new correlation for ammonia, carbon dioxide, and hydrogen sulfide volatilities from aqueous sour water systems has required the completion of the following project objectives:

1. Compare new NH_3-H_2S-H_2O experimental vapor-liquid equilibrium data developed by Brigham Young University with previously published data by Van Krevelen.

2. Check and "fine tune" (if necessary) the new vapor-liquid equilibrium equations developed by Brigham Young University to the measured experimental data.

3. Compare BYU equations to equilibrium expressions previously published by Van Krevelen and Beychok.

4. Modify the BYU equilibrium equations to allow calculations with or without external pH adjustment (i.e., using caustic).

5. Modify the existing BYU computer program to allow equilibrium calculations with or without adjustment.

These objectives have been achieved by first developing a correlation model in which literature data of Van Krevelen, new BYU data, and other literature data have been used to develop equations capable of predicting data over wide ranges in concentration and temperature. Based on these equations a new sour water equilibrium computer program has been developed which is capable of handling the various chemical and physical equilibria of sour water systems including the effects of carboxylic acids or stronger acids on ammonia fixation and release by caustic addition.

This new sour water equilibrium correlation has now been used to evaluate published and new vapor-liquid equilibrium data. Details of the correlating equations, computer program, and data evaluations are given in subsequent sections of this report.

SECTION 3

THE SWEQ MODEL

The SWEQ correlation model developed from this project is very similar to the model used by Van Krevelen (1) except that some of the limitations imposed by that model have been removed. Van Krevelen assumed that H_2S and CO_2 only exist in aqueous solutions as ionized species. This is virtually true at concentrations where NH_3 is in excess, but such an assumption would not be true when these acid gases are present in the absence of NH_3 or other basic components. The method used here, therefore, avoids this problem by considering the chemical equilibrium between ionic species of H_2S or CO_2 and undissociated H_2S or CO_2 in the liquid as follows.

$$H_2S_{(\ell)} \rightarrow HS^- + H^+ \qquad k = \frac{(HS^-)\,(H^+)}{(H_2S)} \qquad (1)$$

$$H_2CO_{3(\ell)} \rightarrow HCO_3^- + H^+ \qquad k = \frac{(HCO_3^-)(H^+)}{(H_2CO_3)} \qquad (2)$$

The SWEQ model not not take into consideration the equilibrium between dissolved CO_2 and carbonic acid (H_2CO_3) according to the following reaction

$$CO_2 + H_2O \rightleftarrows HCO_3 \qquad (3)$$

because the presence of other acidic or basic component does not affect this equilibrium. This reaction is apparently slow enough that the kinetics of absorption of CO_2 into basic aqueous solutions is slower than for H_2S. In spite of this slower reaction rate, the assumption is made here that sufficient contact time or catalyst is used to achieve chemical equilibrium.[a] By this method, the partial pressure of H_2S or CO_2 in the vapor phase above a solution can be calculated from the concentrations of the undissociated species as follows.

---

[a] Because of the slower absorption of CO_2 into water and because of the possibly slow conversion of bicarbonate ion to carbonate ion by excess ammonia, a warning is given that actual plate efficiencies could be low compared to expected efficiencies when CO_2 is present.

$$p_{H_2S} = H_{H_2S} \quad (4)$$

$$p_{CO_2} = H_{CO_2} C_{H_2CO_3} \quad (5)$$

where

p_{H_2S}, p_{CO_2} = partial pressure of H_2S or CO_2

H_{H_2S}, H_{CO_2} = Henry's constants for H_2S and CO_2

C_{H_2S}, $C_{H_2CO_3}$ = liquid phase concentrations of H_2S and H_2CO_3, moles/Kg of solution

The Henry's constant used here must apply at finite concentrations as well as infinitely dilute concentrations, so, in general, H_{H_2S} and H_{CO_2} become dependent on the composition of the solution. This method of calculating H_2S and CO_2 partial pressures is analogous to Van Krevelen's method for calculating ammonia partial pressures which a composition dependent Henry's constant is used. The addition of Henry's constants and undissociated H_2S or H_2CO_3 species concentrations makes possible the calculation of vapor-liquid equilibria at acid gas concentrations in excess of ammonia or of other basic components; thus the Van Krevelen restriction to compositions with excess ammonia is avoided.

This method for calculating vapor-liquid equilibrium data under conditions of simultaneous chemical equilibrium requires two properties that must be correlated in terms of analytical equations as follows.

1. Analytical equations for the effect of temperature and composition on Henry's Law constants so that component partial pressures in the vapor phase can be calculated from calculated concentrations of undissociated NH_3, CO_2, and H_2S in the liquid phase.

2. Analytical equations for the effect of temperature and composition on chemical equilibrium constants so that the concentrations of undissociated NH_3, CO_2, and H_2S in the liquid can be calculated.

Rather than do an exhaustive recorrelation of existing literature data for these properties, an attempt has been made to use existing correlations where possible. Modifications to these existing correlations have been made when necessary to improve the representation of multicomponent data studied in this project. Fortunately, the Henry's constants for NH_3, CO_2, and H_2S can be based primarily on binary data in water. This simplifies the correlation because these properties are fairly well known. Multi-component vapor-liquid data thus serve primarily to establish the effects of high concentrations of the various compounds in solution on these Henry's constants.

By this method, the Henry's constants for ammonia and carbon dioxide at low concentrations of each compound have been taken directly from the literature.

Van Krevelen's correlation was made in terms of component concentrations in moles per liter (ℓ) of solution or molarity. This method introduces an unnecessary variable which is the density of the solution. This occurs because the density is needed to calculate the molarity when the number of moles or number of pounds or grams of each component in a mixture are specified. The SWEQ model avoids this problem by using concentrations in moles/Kg of solution. At low concentrations of the solutes the density of the solution is about one, so the low concentration parameters of Van Krevelen's correlation still apply. However at conditions where the density deviates significantly from unity, then parameters in the two correlations cannot be directly compared. At these conditions, the parameters in the SWEQ model have been determined by directly fitting available phase equilibrium data using concentrations in moles/Kg of solution. By this method there is no ambiguity in the correlation because concentrations in moles/Kg of solution have only been used in the correlation, and the method avoids the need for density at the various concentrations and temperatures of the correlation. At low concentrations of the components, published Henry's constants and chemical equilibrium constants have been used in units of moles/Kg of water because the two sets of units are the same at the zero concentration unit.

Table 1 summarizes the various equations used in the SWEQ model for calculating Henry's constants for NH_3, CO_2, and H_2S. The Henry's constant for ammonia at low ammonia concentrations has been taken directly from the equation of Edwards, Newman, and Prausnitz (3) rather than from Van Krevelen because their correlation is more recent and includes data which was not available to Van Krevelen. Exisiting literature data for the volatility of ammonia from aqueous solutions scatters considerably, but the equation of Edwards et al appears to correlate the data of greated precision.

The Van Krevelen model does not require Henry's constants for CO_2 and H_2S, so these have been obtained from another source. Kent and Eisenberg have recently published correlations (4) on H_2S and CO_2 partial pressures from aqueous monoethanol amine and diethanol amine solutions which appear to correlate these systems quite well. In their correlation they adjusted the amine equilibrium constant for reaction with hydrogen ions to obtain agreement with published data on H_2S and CO_2 partial pressures. By this method they obtained a model capable of accurately predicting equilibrium in H_2S-CO_2-amine systems. Their equations for the Henry's constant for CO_2 has been used without any changes as it is given in Table 1. Their Henry's constant for H_2S however was increased about 12% in order to improve the represenation of multicomponent data by a change in the first constant as noted at the bottom of Table 1.

The use of Henry's constants to correlate volatility data introduces two methods for calculating concentration effects. One method is to assume that the Henry's constant varies with the concentration of the various compounds in solution, and the other method is to assume the various compounds in solution. In some cases, the choice of a concentration parameter in the Henry's constant or of using a concentration parameter in the equilibrium

TABLE 1. SUMMARY OF EQUATIONS USED TO CALCULATE TEMPERATURE AND COMPOSITION EFFECTS ON HENRY'S LAW RELATIONS[a)]

Compound	Lit. Ref.	Fortran Symbol	Equation[b)]
Ammonia	3	HA	$\ln(HA) = 178.339 - 15517.91/T - 25.6767\ \ln(T) + .019660T + (131.4/T - .1682)(CAS) + (.06)(2CC + CS)$
Carbon Dioxide	4	HC	$\ln(HC) = 18.33 - 24895.1/T + .223996 \times 10^{8}/T^{2} - .090918 \times 10^{11}/T^{3} + .12601 \times 10^{13}/T^{4}$
Hydrogen Sulfide	4	HS	$\ln(HS) = 100.684^{*} - 246254/T + 2.39029 \times 10^{8}/T^{2} - 1.01898 \times 10^{11}/T^{3} + 1.59734 \times 10^{13}/T^{4} - .05(CAS) + (.965 - 486/T)(CC)$
Water	13	HW	$\ln(HW)^{c)} = 14.466 - 6996.6/(T-77.67)$

a) T = temperature in °R

CAS = free ammonia concentration, gram-moles/Kg of solution.

CC = total CO_2 in solution, gram moles/Kg of solution.

CS = total H_2S in solution, gram-moles/Kg of solution.

b) Henry's constant in psia/(gram-moles/Kg of solution).

c) Water vapor pressure in psia; the partial pressure in water is calculated from Raoult's Law

*Constant adjusted from 100.573 to 100.684 in order to fit new H_2S solubility data; and multicomponent NH_3-CO_2-H_2S-H_2O data.

constant has been arbitrary. A summary of methods used in the SWEQ model is given in the following.

Compound Affected	Concentration Effects on Volatility Data Correlated by Henry's Const.	Equil. Const.	Principal Data Correlated
NH_3	free NH_3		NH_3-H_2O
	absorbed CO_2		H_2S-CO_2-NH_3-H_2O
	and H_2S		H_2S-NH_3-H_2O
CO_2		absorbed H_2S	H_2S-CO_2-NH_3-H_2O
		ionic strength	CO_2-NH_3-H_2O
H_2S	free NH_3		H_2S-NH_3-H_2O
	absorbed CO_2	absorbed CO_2	H_2S-CO_2-NH_3-H_2O

Van Krevelen used a Henry's constant for ammonia which he assumed to be only dependent on free ammonia concentration. Additional effects of absorbed H_2S and CO_2 were found necessary in the SWEQ model in order to correlate more recent H_2S-CO_2-NH_3-H_2O, so any concentration effects for these compounds in his model correlated in the equilibrium constant.

The effects of free ammonia, and of absorbed H_2S or CO_2 on the Henry's constants used in the SWEQ model are given in Table 1. In this table, the Henry's constant of ammonia is proportional to a constant times CAS, free NH_3, and to a constant times (2 CC + CS), absorbed CO_2 and H_2S. No concentration effects were introduced in the SWEQ model on the Henry's constant of CO_2, but effects for free ammonia and absorbed CO_2 were introduced to correlate H_2S volatility data as shown by terms proportional to CAS and CC in Table 1.

An equation for water is also given in Table 1. Water generally exists as the principal component even in concentrated solutions of electrolytes so that liquid-phase non-ideality effects on the partial pressure of water are small. For this reason, the partial pressure of water in the vapor phase can be calculated from Raoult's Law where the moles of each ionized and unionized species in solution is considered in calculating the mole fraction of water. The partial pressure of water is then calculated from its vapor pressure according to the following equation.

$$p_{H_2O} = p^o_{H_2O}\, x_{H_2O} \qquad (6)$$

where

$p^{o}_{H_2O}$ = vapor pressure of water

x_{H_2O} = liquid phase mole fraction of water

By this method, the constants for water in Table 1 are simply the vapor pressure of water fitted over the range from 25°C to 150°C from data in the steam tables.

No attempt has been made in the SWEQ model to correct for non-ideal behavior in the vapor phase. At low pressures, errors from assuming ideality are probably less than ± 5%; but at pressures of 50 psia or higher, the errors will be greater than this and serious consideration should be made to correct for non-ideal in the vapor phase.

Besides Henry's constants, one must correlate the chemical equilibria of reactions occurring in the liquid phase as mentioned above. The Van Krevelen correlation is limited because the effects of other acidic or basic components cannot be readily taken into account. This problem is avoided in the SWEQ model by assuming that the various chemical equilibria are dependent on the concentrations of either the ionized or undissociated species of a component and the hydrogen ion concentration. For an acid, the general form of the equilibrium equation is as follows:

$$AH \rightarrow A^- + H^+ \qquad k = \frac{(H^+)(A^-)}{AH}$$

while for a base the equilibrium can be written as follows:

$$BOH + H^+ \rightarrow H^+ \rightarrow B^+ + H_2O \; . \qquad k = \frac{(B^+)}{(BOH)(H^+)} \qquad (8)$$

In principle, the assumption of equilibria according to these equations makes possible the calculation of the equilibrium species concentration of each component knowing only the total concentration of that component and the pH. If the pH is not known it can be calculated by trial and error until electrical neutrality is achieved in a given mixture of compounds. This method of calculation permits the development of generalized calculation methods, so that new compounds can be added as necessary. In many respects the method is similar to an equilibrium flash calculation where the feed composition and equilibrium K-values of individual components are known. In a flash calculation, the concentrations of each component in the vapor and liquid phase is known. But in general, the fraction as vapor or liquid is not known so an iterative calculation is made until the concentrations in each phase add to 100%. For acid-base equilibria, the problem is nearly as simple except that the iteration parameter is pH instead of fraction as vapor or liquid. The picture for H_2S and CO_2 is slightly more complicated because both components have second ionization constants so that two chemical reactions must be simultaneously solved at a given pH value. In this case, a calculation example is given as follows.

$$AH_2 \rightarrow AH^- + H^+ \qquad k_1 = \frac{(AH^-)(H^+)}{(AH)} \tag{9}$$

$$AH^- \rightarrow A^= + H^+ \qquad k_2 = \frac{(A^=)(H^+)}{(AH^-)} \tag{10}$$

To solve these equations, it is assumed that the total concentration of both ionized plus undissociated species concentrations is known by chemical analysis; but that the concentration of each individual species is not known. In this case, the concentrations of individual species can be related by the following equations.

$$(AH_2) = n_A - \alpha - \beta \tag{11}$$

$$(AH^-) = \alpha \tag{12}$$

$$(A^=) = \beta \tag{13}$$

From these equations, the following equations are obtained for k_1 and k_2.

$$k_1 = \frac{(\alpha)(H^+)}{(n_A - \alpha - \beta)} \tag{14}$$

$$k_2 = \frac{(\beta)(H^+)}{(\alpha)} \tag{15}$$

These simultaneous equations can be algebraically solved for α and β to give the following equations.

$$\alpha = \frac{k_1 n_A}{(H^+) + k_1 + k_1 k_2/(H^+)} \tag{16}$$

$$\beta = \frac{k_1 k_2 n_A/(H^+)}{(H^+) + k_1 + k_1 k_2/H^+} \tag{17}$$

If no second ionization occurs, then k_2 is zero and α becomes as follows.

$$\alpha = \frac{k_1 n_A}{(H^+) + k_1} \tag{18}$$

After α and β have been calculated from equations 16 and 17, then the concentration of undissociated species can be calculated from equation 11. Because of computer round-off error due to subtracting two large numbers to get a small number, it has been found better to calculate the undissociated species concentration from equation 14 instead of equation 11. This is done by rearranging equation 14 to the following equation in which the round-off error ia avoided.

$$n_A - \alpha - \beta = (AH_2) = (\alpha)(H^+)/k_1 \tag{19}$$

The calculation of chemical equilbria in mixtures containing both ammonia and carbon dioxide requires allowance for the reaction of bicarbamate ion with free ammonia to produce carbamate ion as follows.

$$HCO_3^- + NH_3 \rightarrow H_2NCOO^- + H_2O \qquad (20)$$

$$k = \frac{(H_2NCOO^-)}{(HCO_3^-)(NH_3)}$$

This introduces a third simultaneous reaction for CO_2 and a second simultaneous reaction for NH_3. This added complexity makes necessary a second iterative calculation procedure to calculate individual species concentrations at a specified pH value. This calculation is made by assuming various bicarbonate concentrations from which the concentrations of the other species can be algebraically calculated. The resulting concentrations of individual CO_2 species are then added compared with the specified moles of CO_2 in the solution as follows.

$$n_{CO_2(calc)} = (CO_2) + (HCO_3^-) + (CO_3^=) + (H_2NCOO^-) \qquad (21)$$

The amount of carbonate is then adjusted up or down by the following ratio.

$$(HCO_3^-)_{new} = (HCO_3^-)_{old} \frac{(n_{CO_2})_{actual}}{(n_{CO_2})_{old}} \qquad (22)$$

Fortunately, this iteration method appears to converge after only town or three iterations.

This discussion of chemical equilibria involving H_2S, CO_2, NH_3, and water outlines the details of various steps used in the SWEQ model[3] to calculate the concentration of each individual species in solution. Table 2 gives a summary of the various reactions which are accounted for by the model. There are a total of eight reactions listed in this table. First ionization constants are involved in reactions 1, 3, 5, 7, and 8; and second ionization constants are involved in reactions 2 and 6. In addition, bicarbonate ions react with ammonia to produce carbamate ions in reaction 4. The corresponding equilibrium equations based on the extent of each reaction occurring are given to the right for each reaction in Table 2. Except for reaction number 4 for carbamate formation, the equilibrium concentrations of each species are shown to be proportional to the pH of the solution. If the pH is known, it becomes a rather easy matter to compute the equilibrium concentration of each species in solution. If the pH is not known, an iterative method has to be devised as discussed above whereby an initial pH is assumed. Then as steps in the iteration loop, the concentration of each species is calculated by calculating the extent of each chemical reaction. From the calculated species concentrations the sum of all electronic charges HT can then be cal-

culated by the equation shown at the bottom of Table 2. Generally this sum will not be zero, but the assumed pH can then be adjusted to bring the sum closer to zero thus forming a closed iteration loop. Iteration can then be formed until the two values agree within a small tolerance. This calculation method is very convenient and powerful because it can be readily expanded to include other basic compounds as future needs arise.

A rigorous thermodynamic approach to the problem of calculating chemical equilibria in electrolyte solutions involves the use of activity coefficients for each species in solution requiring interaction parameters between each species. These activity coefficients are then used to calculate the effect of composition and ionic strength on the chemical equilibrium constants. Such a method has been proposed by Edwards, Newman, and Prausnitz (3) for aqueous solutions of volatile weak electrolytes. However, because of assumptions in their model, their correlation is not suitable for concentrated solutions of these compounds.[a] To avoid this problem and to minimize computer time required for calculating the activity coefficient of each individual species, a more empirical method was used for the SWEQ model.

In the SWEQ model, the equilibrium constants in Table 2 are assumed to be given by equations of the following form.

$$\ln K_i = \ln K_i^o + aC_{H_2S} + bC_{CO_2} + c\, I^{0.4} \qquad (23)$$

where K_i = equilibrium constant

K_i^o = equilibrium constant at infinite dilution of all species

a,b,c = parameters

C_{H_2S} = Total moles H_2S absorbed/Kg of solution

C_{CO_2} = Total moles CO_2 absorbed/Kg of solution

I = ionic strength = $1/2\ \Sigma_i C_i Z_i^2$, Z_i = ionic charge

The constant a and b have been found to be independent of temperature while c is found to be dependent on temperature. In many respects, this empirical

---

[a] A paper was given by Edwards, Newman, and Prausnitz at the 70th AICHE Meeting, New York Session, 13-17 November 1977, on "Vapor-Liquid Equilibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes." They report a new correlation similar to their first paper, [4] but the range of application has been extended to temperatures from 0 to 170°C (32 to 338°F) and total solute concentrations up to 10 molal. This new work was published as the final report of this project was being written, so no comparisons with the SWEQ model have been made.

TABLE 2. SUMMARY OF CHEMICAL EQUILIBRIA INVOLVED IN CALCULATING NH_3-CO_2-H_2S-H_2O VAPOR-LIQUID EQUILIBRIA

Chemical Reaction	Equilibrium Constant*
1. $\underset{n_C-\alpha-\beta-\varepsilon}{CO_2} + H_2O \rightarrow \underset{\alpha}{HCO_3^-} + H^+$	$k = \frac{(H^+)\,\alpha}{(n_C-\alpha-\beta-\varepsilon)}$
2. $\underset{\alpha}{HCO_3^-} \rightarrow \underset{\beta}{CO_3^=} + H^+$	$k = \frac{(H^+)\,\beta}{\alpha}$
3. $NH_3 + H^+ \rightarrow \underset{\delta}{NH_4^+}$ $n_A-\delta-\varepsilon$	$k = \frac{\delta}{(H^+)\,(n_A-\delta-\varepsilon)}$
4. $NH_3 + HCO_3^- \rightarrow \underset{\varepsilon}{H_2NCOO^-} + H_2O$ $n_A-\delta-\varepsilon \quad \alpha$	$k = \frac{\varepsilon}{\alpha(n_A-\delta-\varepsilon)}$
5. $H_2S \rightarrow \underset{\gamma}{HS^-} + H^+$ $n_S-\gamma-\psi$	$k = \frac{(H^+)\,\gamma}{n_S-\gamma-\psi}$
6. $\underset{\gamma}{HS^-} \rightarrow \underset{\psi}{S^=} + H^+$	$k = \frac{(H^+)\,\psi}{\gamma}$
7. $H_2O \rightarrow H^+ + OH^-$ $(\sigma + CCAU)$	$k = (H^+)(\sigma + CCAU)$
8. $RCOOH \rightarrow \underset{\zeta}{RCOO^-} + H^+$ $n_{sA}-\zeta$	$k = \frac{\zeta(H^+)}{n_{sA}-\zeta}$

*The sum of all electronic charges is given as follows: $(HT) = \alpha + 2\beta - \delta + \gamma + 2\psi + \sigma + \varepsilon + \zeta - CCAU - H^+$

method is similar to the method used by Van Krevelen. Van Krevelen found that the equilibrium constants for reaction of H_2S and CO_2 with NH_3 were proportional to ionic strength, so a single correlation parameter was introduced to account for this effect. This has been changed slightly in the SWEQ model in order to predict multicomponent equilibrium data at high concentrations by introducing a and b as additional parameters for the separate effects of absorbed CO_2 and H_2S. Actual parameters used in the SWEQ model are summarized in Table 3. This table shows that only three coefficients have been introduced. A multiplying factor of -.278 times the concentration of absorbed H_2S and a temperature function time the ionic strength appear for the first dissociation constant of CO_2 as given by reaction 1 in Table 3. The effect of ionic strength has been taken directly from Figure 3 of Van Krevelen's papers by fitting the curves in his plot to an analytical equation of the following form

$$(\text{Effect of ionic strength on } \ln K) = CI^n \qquad (24)$$

where C = temperature dependent parameter

n = empirical exponent (a value of 0.4 was found although a value of 0.5 would be more correct from Debeye-Huckel considerations)

Van Krevelen's correlation was made in terms of the following reaction.

$$CO_{2(g)} + H_2O_{(e)} + NH_{3(e)} \rightleftarrows HCO_3^- + NH_4^+ \qquad (25)$$

$$\text{where } K_{V.K.} = \frac{(HCO_3^-)(NH_4^+)}{(P_{CO_2})(NH_3)}$$

This equilibrium constant can be rewritten in terms of a Henry's constant for CO_2 as follows.

$$K_{V.K.} = \frac{(HCO_3^-)(NH_4^+)}{(H_{CO_2})(H_2CO_3)(NH_3)} \qquad (26)$$

From Table 2, this represents the sum of reactions 1 and 3 as follows.

$$K_{V.K.} = \frac{(K_1)(K_3)}{(H_{CO_2})} \qquad (27)$$

In the SWEQ model, it is assumed that H_{CO_2} and k_3 are independent of composition; thus any effect of ionic strength of ionic strength on $K_{V.K.}$ becomes a similar effect on K_1.

The term of $-0.278\ C_{H_2S}$ in Table 3 has resulted from fitting CO_2 partial pressures data from quarternary H_2S-CO_2-NH_3-H_2O mixtures measured at Brigham Young University. (5) It does not affect ternary CO_2-NH_3-H_2O data and only

TABLE 3. EFFECT OF COMPOSITION AND IONIC STRENGTH ON CHEMICAL EQUILIBRIUM CONSTANTS[a]

$$\ln K_i = \ln K_i^\circ + aC_{H_2S} + bC_{CO_2} + cI^{0.4}$$

where K_i° = equilibrium constant at infinite dilution of all species

a,b,c = parameters

C_{H_2S}, C_{CO_2} = total moles of H_2S or CO_2 absprbed in one Kg of solution

$I = 1/2\ \Sigma_i C_i Z_i^2$ = ionic strength

Z_i = ionic charge

Chemical Reaction in Table 2	a	b	c
1	-.278	0	-1.32 + 1558.8/T°R
2	0	0	0
3	0	0	0[b]
4	0	0	0
5	0	.427	0
6	0	0	0
7	0	0	0
8	0	0	0

[a] The equation and constants given here are discussed in the section on the SWEQ model, equation 23.

[b] No effect of ionic strength is required for NH_3 because its equilibrium constant is used in combination with either H_2S or CO_2.

becomes important when significant concentrations of both CO_2 and H_2S are present. The third coefficient in Table 3 appears as a multiplying factor of 0.427 times the concentration of absorbed CO_2 which affects the first dissociation constant of H_2S as given by reaction 5 in Table 3. This effect was also found necessary besides concentration terms in the Henry's constant to correlate the quarternary H_2S-CO_2-NH_3-H_2O data. Van Krevelen found that a multiplying factor of 0.089 times ionic strength to be necessary in $\log_{10}$ K. In the SWEQ model, this is accounted for in the concentration-dependent terms of the H_2S Henry's constant given in Table 1.

The concentration effects given in Tables 1 and 3 were developed in the following steps:

1. Binary NH_3-H_2O data were correlated to obtain the effect of free NH_3 on the Henry's constant of NH_3.

2. Binary H_2S-H_2O and ternary H_2S-NH_3-H_2O data were correlated to obtain an adjusted zero concentration Henry's constant of H_2S as noted at the bottom of Table 1, and an additional concentration parameter proportional to free NH_3 concentration for the Henry's constant of H_2S was introduced as shown in Table 1. The chemical equilibrium constant of reaction 3 in Table 2 for the combination of NH_3 plus H^+ to give (NH_4^+) was also adjusted as an empirical parameter in order to fit the H_2S-NH_3-H_2O data. It was also found necessary to introduce an effect of absorbed H_2S on the Henry's constant of NH_3 in order to correlate the ternary data. Thus four effects were correlated:

    a) The zero concentration Henry's constant of H_2S

    b) The effect of free NH_3 on the Henry's constant of H_2S

    c) The equilibrium constant of $NH_3 + H^+ \rightarrow NH_4^+$

    d) The effect of absorbed H_2S on the Henry's constant of NH_3.

3. Binary CO_2-H_2O and ternary CO_2-NH_3-H_2O data were correlated. The effects of ionic strength on the first dissociation constant of CO_2 was used directly from Van Krevelen's correlation. The available data appear to be suitably correlated by this one effect so no new additional concentration parameters were introduced. However, the zero concentration dissociation constant of CO_2 was adjusted slightly in order to obtain an improved representation of the CO_2-NH_3-H_2O data. The equilibrium constant for the reaction of HCO_3^- and NH_3 to produce H_2NCOO^- carbamate ions in reaction 4 of Table 1 was not changed from Van Krevelen's correlation.

4. Quarternary H_2S-CO_2-NH_3-H_2O data were correlated to obtain the effect of absorbed H_2S on the first dissociated constant of H_2CO_3 and the effect of absorbed CO_2 on the Henry's constant of H_2S and on the first dissociation constant of H_2S.

Comparisons between measured and calculated data are given in a subsequent section of this report.

The chemical equilibrium constants for the reactions given in Table 2 are dependent on temperature. This effect is calculated in the SWEQ model from equations of the same form given by Kent and Eisenberg (4) as follows.

$$\ln K_i^o = A + B/T + C/T^2 + D/T^3 + E/T^4 \qquad (28)$$

where T is in degrees Rankine and concentrations are in gram moles or gram ions/Kg of solution. Actual parameters used are given in Table 4. In many cases the parameters are the same as the ones used by Kent and Eisenberg (4). Various changes were made in these constants as noted at the bottom of Table 4. These changes were as follows.

1. The reaction constant of $NH_3 + H^+ \rightarrow NH_4^+$ was first adjusted empirically using available H_2S-NH_3-H_2O volatility data and the equilibrium constant of H_2S as published by Kent and Eisenberg.

2. The reaction constants for the first and second ionization constants of CO_2 were adjusted from Kent and Eisenberg's equations to fit available CO_2-NH_3-H_2O data. This was done so as not to affect the H_2S-NH_3-H_2O correlation.

3. After Parts 1 and 2 were done it was found by detailed comparisons of measured and calculated data given in subsequent tables of this report that both the H_2S and CO_2 volatility data could be adjusted slightly to improve their predicted values. This was done by changing the first dissociation constants of H_2S and CO_2. The original constant for NH_3 was left unchanged. The net effects of these various changes are noted at the bottom of Table 4.

The equilibrium constant of NH_3 reacting with HCO_3^- to produce H_2NCOO^- carbamate ion was used as published by Van Krevelen. The dissociation constant of H_2O was used as published by Kent and Eisenberg (4). The ionization constant of carboxylic acids (RCOOH) in water (H_2O) are nearly independent of temperature thus a single constant is used for RCOOH ionization according to reaction 8 in Table 2. The value of -11.28 is based on a pK_a of about 4.9 reported by Bomberger and Smith[6] from potentiometric titrations of actual refinery sour water streams. This reaction has been introduced into the calculation method so that the effect of carboxylic acids on the volatility of NH_3 can be calculated. A molecular weight of 60.05 is assumed in the SWEQ calculation model, but another value could be entered if necessary. The amount of carboxylic acid in a given sour water stream can be obtained from a

TABLE 4. SUMMARY OF TEMPERATURE PARAMETERS, USED TO CALCULATE CHEMICAL EQUILIBRIUM CONSTANTS IN TABLE 1

($\ln K_1^\circ = A + B/T + C/T^2 + D/T^3 + E/T^4$ for T in °R, and concentrations in gram moles or gram ions per Kg of soln.)

Chemical Reaction in Table 2	Lit Ref	Temperature Parameters				
		A	B	C	D	E
1	4,7,8	-241.79*	536256*	-4.8123×10^8	1.94×10^{11}	-2.96445×10^{13}
2	4,7,8,9	-295.60*	655893	-5.9667×10^8	2.4249×10^{11}	-3.7192×10^{13}
3	*	1.587*	11160*	0	0	0
4	1	-5.40	3465	0	0	0
5	4,11,12	-293.88*	683858*	$-6.27125 \times 10^{8*}$	2.555×10^{11}	-3.91757×10^{13}
6	4,11,12	-657.965	1649360	-15.8964×10^8	6.72472×10^{11}	-10.6043×10^{13}
7	4,10	39.5554	-177822	1.843×10^8	$-.8541 \times 10^{11}$	1.4292×10^{13}
8	6	-11.28	0	0	0	0

*Adjusted to fit experimental data. The following is a comparison of correlated K's with literature K°'s for reactions 1, 3, and 5.

Ionization	Reaction	Literature Values		K/K_{lit}	
		A	B	180°F	240°F
H_2CO_3	1	-241.818	536855	.40	.44
HCO_3^-	2	-294.740	655893	.42	.42
H_2S	5	-304.689	696979	.81	.99

(C also adjusted from -6.31007×10^{-8})

The reaction of $NH_3 + H^+ \rightarrow NH_4^+$ was adjusted empirically as was done by Kent and Eisenberg[4] for amines. H_2S-NH_3 data were fitted first so the changes in the H_2S dissociation constant were primarily temperature effects. When CO_2 data were correlated, its ionization constant was adjusted so as not to affect the H_2S-NH_3-H_2O correlation.

potentiometric titration of samples taken from the stream as performed by Bomberger and Smith. This information can then be used to calculate the amount of caustic to be added in order to release the NH_3.

In the SWEQ model, the volatilities of H_2S, CO_2, or NH_3 in solution are dependent on the H^+ ion concentration or pH of the solution. This effect is shown in Figure 1 where the ratio of vapor over liquid concentrations on a weight-%-basis are plotted at 120°C (or about 30 psia) versus pH measured at 25°C. These data were calculated assuming a 0.01 weight-% concentration in the liquid phase. From this plot, we see that H_2S and CO_2 have greater volatilities at low pH levels while NH_3 has greater volatilities at high pH levels. This means that a process for simultaneous stripping of all three components from solution must operate at an intermediate pH where all three have reasonable volatilities. From this plot, the optimum pH measured at 25°C appears to be around 10, but we find that it varies depending on the mixture involved. The equilibrium-constant parameters in Tables 3 and 4 and the Henry's law equations in Table 1 give all the parameters necessary for predicting vapor-liquid data in NH_3-CO_2-H_2-H_2O systems. Other acidic or basic components could be added to the correlation simply by adding parameters for the added components to these tables and by incorporating them into the computer program.

Details of a computer program based on the SWEQ model and comparisons with literature data are given in the next sections of this report.

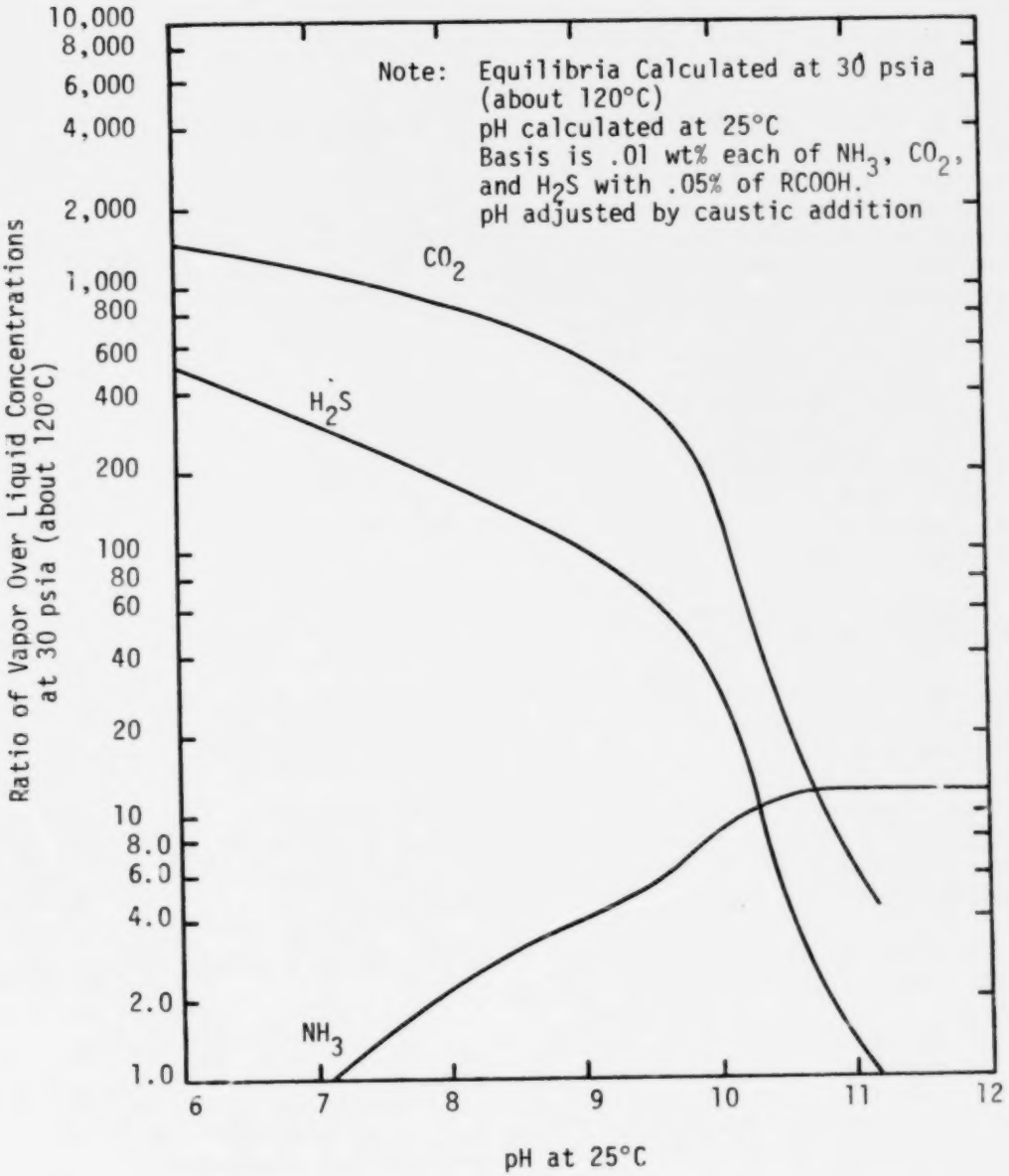

Figure 1. Sample plot of the volatility of NH_3, CO_2, and H_2S versus pH determined by caustic addition.

SECTION 4

COMPUTER PROGRAM BASED ON THE SWEQ MODEL

A computer program for calculating NH_3, CO_2, abd H_2S volatility data from aqueous sour water systems has been developed based on the SWEQ model. The program is written to handle a wide range of conditions and temperatures. The estimated ranges of applicability are as follows:

Property	Range
Temperature	20^oC to 140^oC
Pressure	up to 50 psia*
Composition	1 ppm to about 30 weight % dissolved NH_3, carboxylic acid, salts, and caustic
pH	2 to 14

*Corrections for vapor phase non-ideality are recommended at pressures above 50 psia.

As presently written, the program will handle NH_3, CO_2, H_2S, and water plus NH_3 fixation effects due to carboxylic or stronger acids and the effects of caustic addition.

This computer program uses the new vapor-liquid equations presented in the previous section of this report which were developed from both old and new experimental data. This same program was used to develop data comparisons given in the next section of this report.

The main features of the SWEQ model as it has been programmed are as follows:

1. As shown in the next section, it is more precise than the Van Krevelen method of prediction. This improvement is primarily due to the use of actual data at the conditions of commercial interest for development of the SWEQ model while the Van Krevelen correlation is used at extrapolated conditions.

2. The program will take into account NH_3 fixation effects due to carboxylic acids in sour water systems.

3. The program will also take into account caustic addition to release fixed NH_3.

4. The program can be readily converted to a subroutine for equilibrium stage calculations for various separation processes. Calculations can be made going either up or down in a distillation process.

5. The SWEQ model can be expanded to additional acidic or basic components with only minor changes to introduce new ionization constants and Henry's constants.

Various options in the computer program are available to the user as follows.[a]

1. Option 1 allows the calculation of vapor-liquid equilibrium data at a specified temperature and liquid composition. This option would be used for circumstances in which the temperature at liquid vapor equilibrium is known rather than the pressure. This was the option used in correlating available experimental data of this project. It may also be useful in some process situations.

2. Option 2 allows the calculation of vapor-liquid equilibrium data at a specified pressure and liquid composition. This option would normally be used for equilibrium stage process calculations going up a distillation tower. The program calculates the temperature and vapor composition from a given stage. The pressure change from stage to stage must be controlled by the user in specifying the pressure of the equilibrium calculation.

3. Option 3 allows the calculation of vapor-liquid equilibrium data at a specified pressure and vapor composition. This option would normally be used for equilibrium stage process calculations going down a distillation tower. The program calculates the temperature and liquid composition from a specified vapor composition and pressure. This option would normally be used for sour water stripper calculations. The pressure increment between stages must be controlled by the user in each pressure specified to the program. Option 3 also calculates water in the condenser vapor at a specified pressure, temperature, and vapor stream composition on a water-free basis. In this case, a zero water content is specified as input data for the calculation. This response for zero water content only occurs with Option 3.

Ammonia fixation and caustic addition effects can be calculated with all three options given above. Ammonia fixation effects can be calculated by entering as data a specified wt. % of carboxylic acids in the liquid

---

a) Besides the three options listed here, a fourth option for a flash calculation has been completed. This was done after this report was written, so the results are not in this report. Please contact the author for the details.

analysis. The amount to be entered may be determinable from a potentiometric titration of the sour water under study. The method of titration could be the same or similar to that used by Bomberger and Smith (6). A molecular weight of 60.05 is assumed in the computer program. This number was assumed without any real basis and can be changed in the program without affecting other parts of the program. The effect of caustic addition can be calculated in two ways as follows:

1. If a negative pH is specified as input data, then the program ignores the entry and calculates the pH based in the amount of caustic in wt % specified in the input data. The input concentration refers to the liquid phase even when option 3 is used for calculating down a distillation tower.

2. If a positive pH is specified as input data then the program computes the amount of caustic necessary to obtain the specified pH. In this case, the concentration of caustic specified in the input data is set to zero.

Both of these pH options use or compute pH data at the temperature of the equilibrium stage. If the pH of the liquid at 25°C is desired, the user must specify this temperature and the liquid composition obtained from a higher-temperature equilibrium stage calculation. This would involve the use of distillation option number 1.

Table 5 gives a flow chart of the main program. The format for entry of data to the program is the same regardless of the options used. The basic program involves the reading of input data which then converts the data so it can be processed by options 1, 2, or 3 in the program. After these options, the calculated equilibrium data are then printed by the program.

Flow charts for options 1, 2, and 3 are given in Figures 3, 4, and 5 respectively. These options primarily act as executive programs which call various subroutines necessary to perform the calculations. Iteration loops are involved in each of the options because of the problem of calculating simultaneous chemical equilibria at each condition. The primary interation of pH is done in each option by calculating equilibrium concentrations of each species at assumed pH values. Initially chosen pH values are arbitrary so a test is made to check for electrical neutrality of the solution. For an arbitrary pH, neutrality will not occur; so then a new pH is chose in subsequent iterations until electrical neutrality within a small tolerance is achieved.

A direct listing of the main program is given in Table 5, and listings of the various subroutines used by the main program are given in Tables 6 to 15. These subroutines and their functions are as follows:

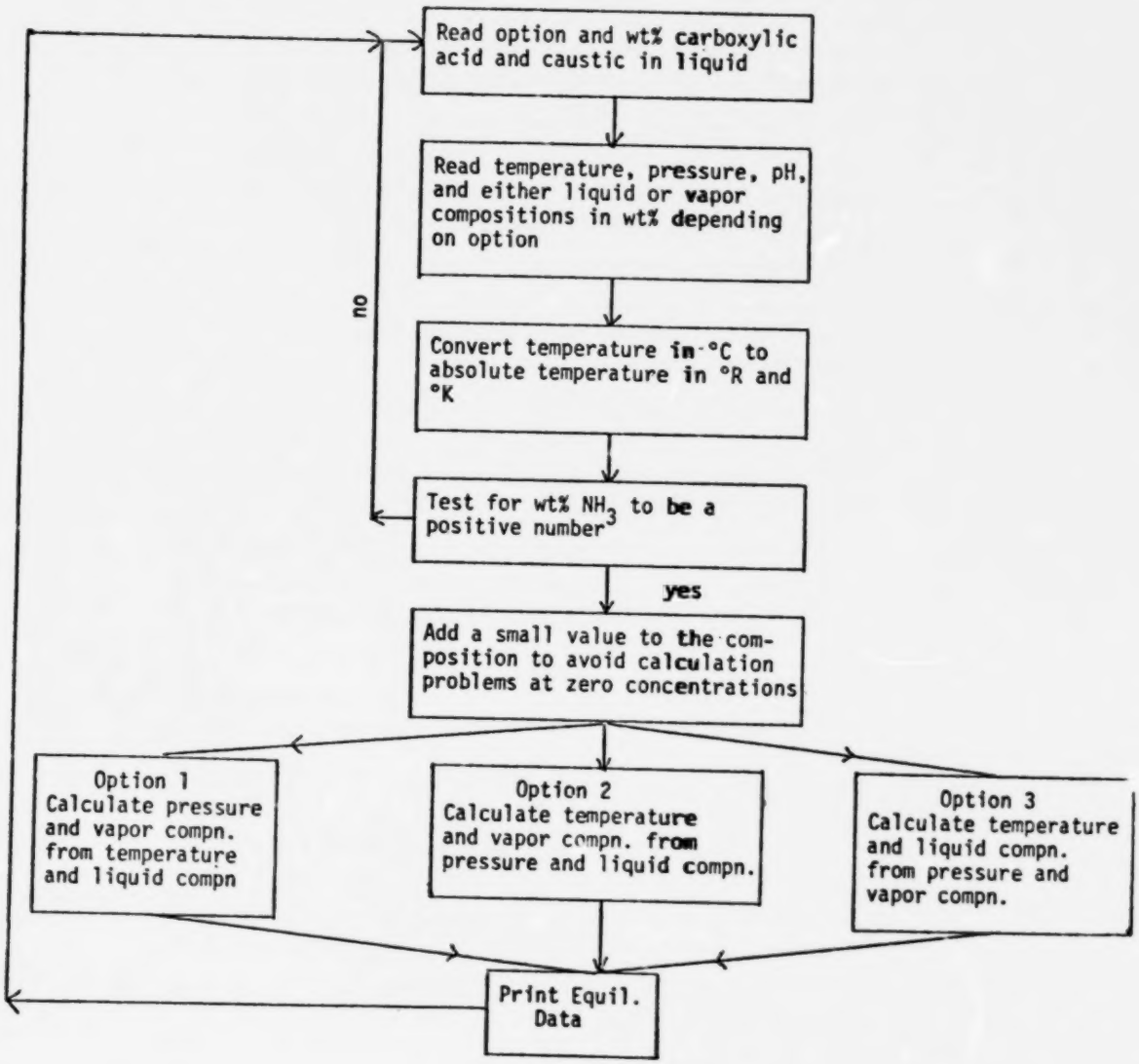
Read option and wt% carboxylic acid and caustic in liquid
Read temperature, pressure, pH, and either liquid or vapor compositions in wt% depending on option
Convert temperature in °C to absolute temperature in °R and °K
Test for wt% NH_3 to be a positive number
no
yes
Add a small value to the composition to avoid calculation problems at zero concentrations
Option 1
Calculate pressure and vapor compn. from temperature and liquid compn
Option 2
Calculate temperature and vapor compn. from pressure and liquid compn.
Option 3
Calculate temperature and liquid compn. from pressure and vapor compn.
Print Equil. Data

Figure 2. Flow diagram of SWEQ main program.

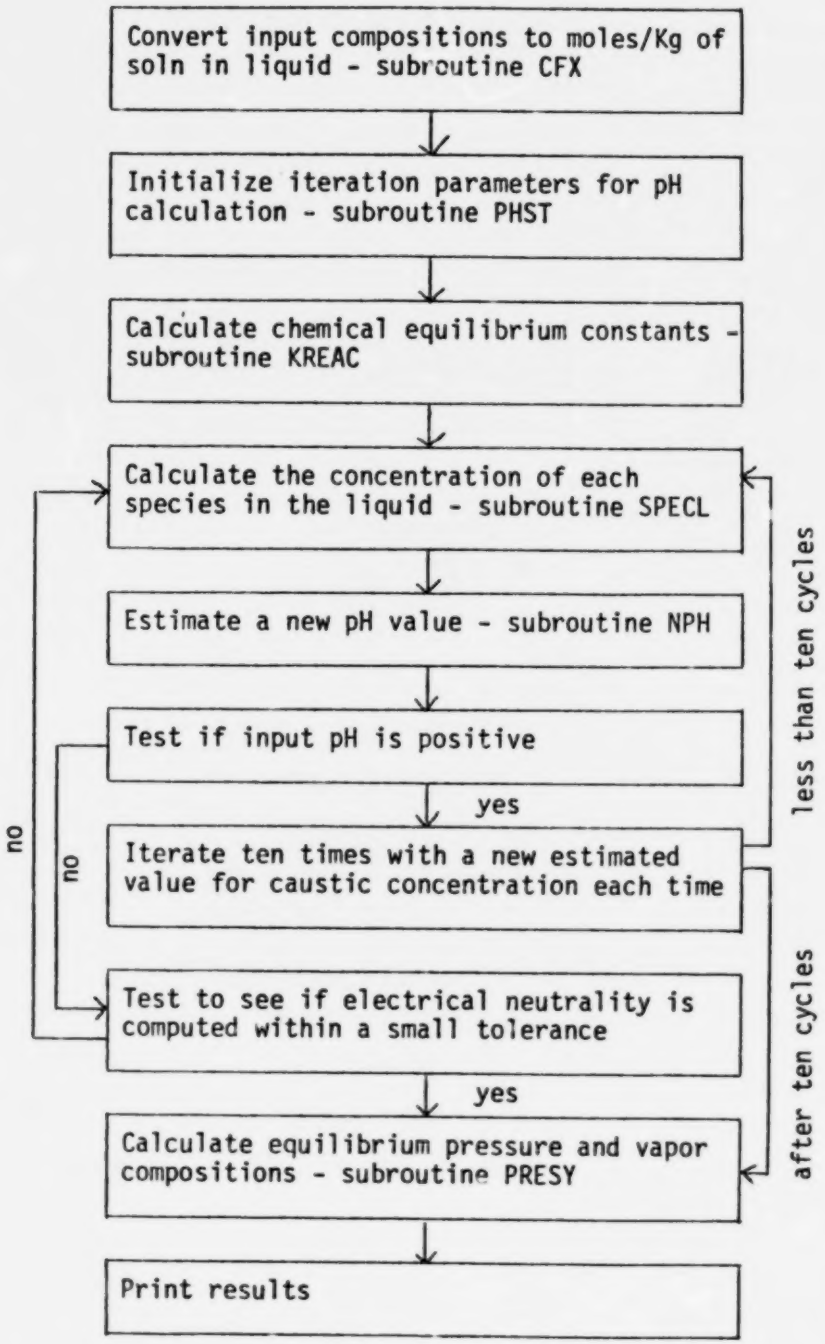
Convert input compositions to moles/Kg of soln in liquid - subroutine CFX
Initialize iteration parameters for pH calculation - subroutine PHST
Calculate chemical equilibrium constants - subroutine KREAC
Calculate the concentration of each species in the liquid - subroutine SPECL
Estimate a new pH value - subroutine NPH
Test if input pH is positive
yes
Iterate ten times with a new estimated value for caustic concentration each time
Test to see if electrical neutrality is computed within a small tolerance
yes
Calculate equilibrium pressure and vapor compositions - subroutine PRESY
Print results
no
no
less than ten cycles
after ten cycles

Figure 3. Flow diagram of option 1 of SWEQ computer program.

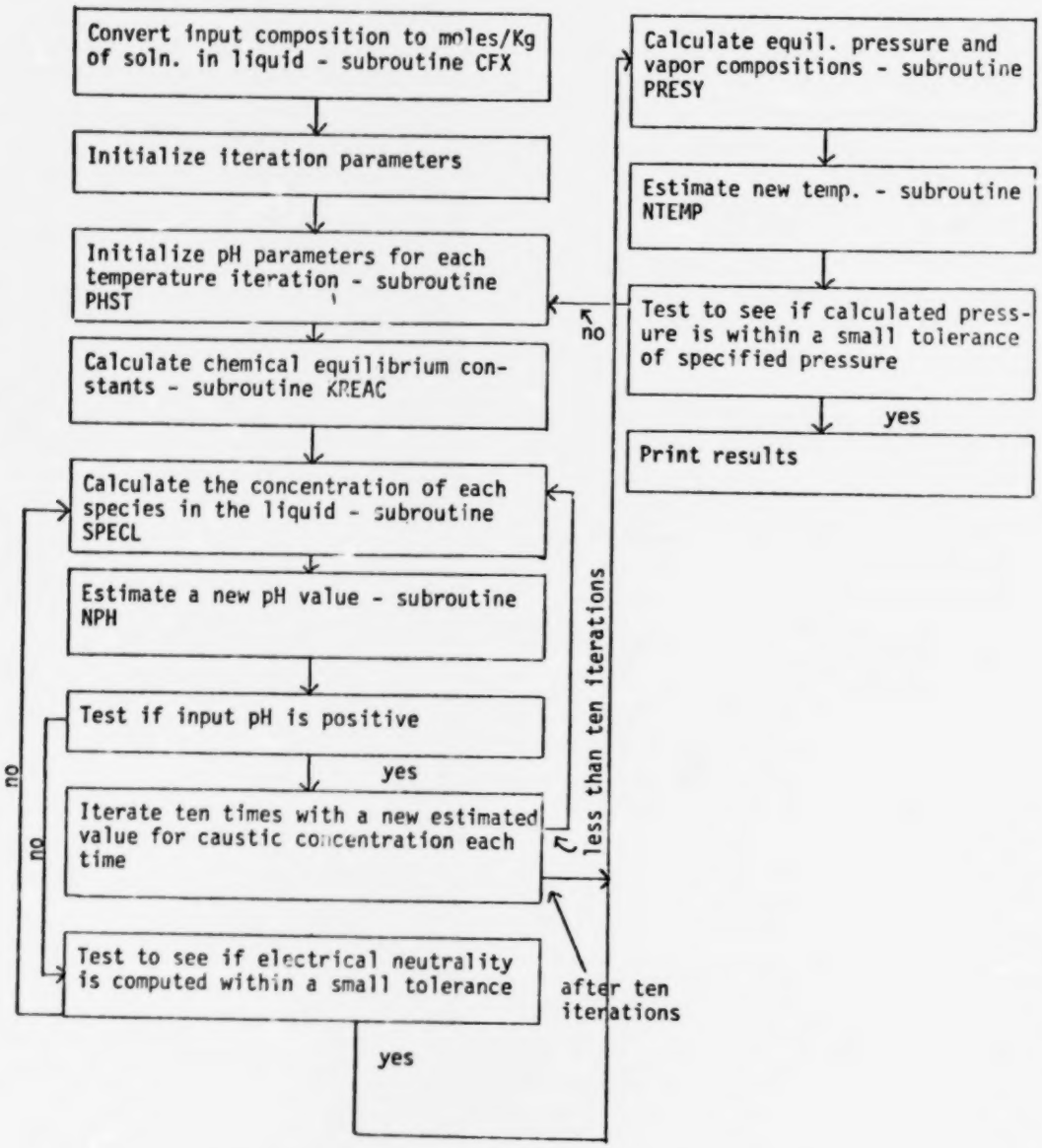
Convert input composition to moles/Kg of soln. in liquid - subroutine CFX
Initialize iteration parameters
Initialize pH parameters for each temperature iteration - subroutine PHST
Calculate chemical equilibrium constants - subroutine KREAC
Calculate the concentration of each species in the liquid - subroutine SPECL
Estimate a new pH value - subroutine NPH
Test if input pH is positive
yes
no
Iterate ten times with a new estimated value for caustic concentration each time
less than ten iterations
after ten iterations
Test to see if electrical neutrality is computed within a small tolerance
no
yes
Calculate equil. pressure and vapor compositions - subroutine PRESY
Estimate new temp. - subroutine NTEMP
Test to see if calculated pressure is within a small tolerance of specified pressure
no
yes
Print results

Figure 4. Flow diagram of option 2 of SWEQ computer program.

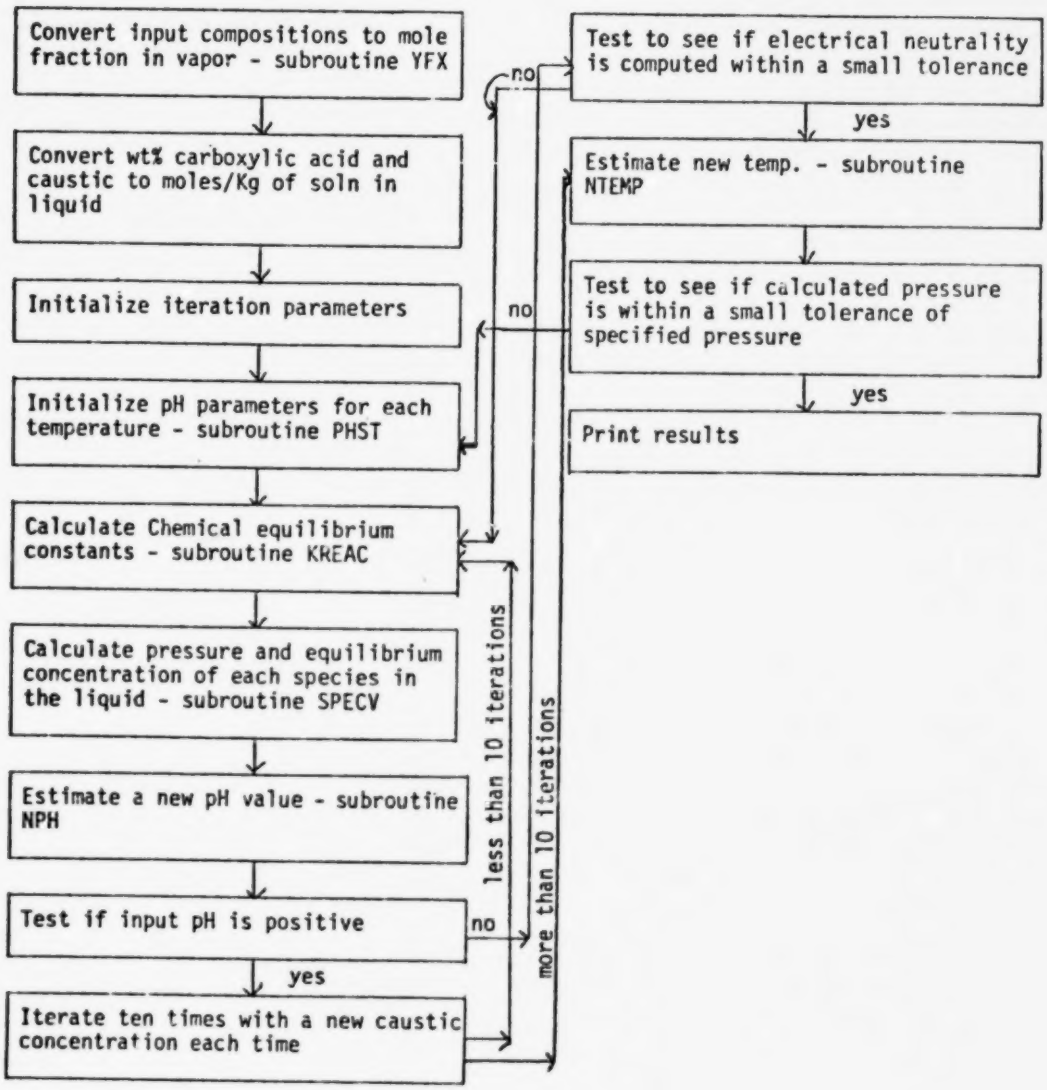
Convert input compositions to mole fraction in vapor - subroutine YFX
Convert wt% carboxylic acid and caustic to moles/Kg of soln in liquid
Initialize iteration parameters
Initialize pH parameters for each temperature - subroutine PHST
Calculate Chemical equilibrium constants - subroutine KREAC
Calculate pressure and equilibrium concentration of each species in the liquid - subroutine SPECV
Estimate a new pH value - subroutine NPH
Test if input pH is positive
no
yes
Iterate ten times with a new caustic concentration each time
less than 10 iterations
more than 10 iterations
Test to see if electrical neutrality is computed within a small tolerance
no
yes
Estimate new temp. - subroutine NTEMP
Test to see if calculated pressure is within a small tolerance of specified pressure
no
yes
Print results

Figure 5. Flow diagram of option 3 of SWEQ computer program.

Reproduced from best available copy.

TABLE 5. COMPUTER PROGRAM BASED ON THE SWEQ MODEL

```
C       SWEQ COMPUTER PROGRAM
C THIS COMPUTER PROGRAM WAS WRITTEN BY GRANT M. WILSON FOR THE API CREC
C COMMITTE, RONALD G. GANTZ SOUR WATER STRIPPER PROJECT MANAGER. QUESTIONS
C ABOUT THIS PROGRAM SHOULD BE DIRECTED TO EITHER GRANT M. WILSON OR RONALD
C G. GANTZ. THIS PROGRAM IS WRITTEN IN FORTRAN FOR OPERATION ON A TIME
C SHARE TERMINAL CONNECTED TO A DIGITAL EQUIPMENT CO.MODEL 10 COMPUTER.
C IT CAN BE CONVERTED FOR USE AS A SUBROUTINE OR FOR BATCH OPERATION. FOR
C OPERATION AS A SUBROUTINE THE ERROR MESSAGES NOW PRINTED ON THE TERMINAL
C WOULD HAVE TO BE CHANGED SO THAT THE EXECUTIVE PROGRAM WOULD TAKE
C CORRECTIVE ACTION. ERROR MESSAGES ARE NOW PRINTED BY STATEMENTS 320, 420,
C AND 515 IN THE MAIN PROGRAM; AND BY STATEMENTS 12 AND 35 IN SUBROUTINE
C SPECV AND BY STATEMENT 7341 IN SUBROUTINE SPECL.
C THIS PROGRAM CALCULATES EQUILIBRIUM VAPOR-LIQUID COMPOSITIONS FOR WEAK
C ELECTROLYTE MIXTURES CONTAINING NH3,CO2,H2S,RCOOH,CAUSTIC, AND WATER.
C COMMENTS IN THE PROGRAM DESCRIBE VARIOUS OPTIONS POSSIBLE AND THE FUNCTION
C OF VARIOUS PARTS OF THE PROGRAM
      COMMON IC,TK,TR,PSI,P,XA,XC,XS,XW,CA,CC,CS,CAS,CCS,CSS,
     1YA,YC,YS,YW,WA,WC,WS,WW,PHO,PH,TOL,HT,DPH,PHA,PHB,AL,BT,GA,
     2DE,SI,HP,SD,EPS,EKS,EKCA,EKCAO,EKCB,EKA,EKW,EKCC,EKSB,EKSA,HTO,
     3EL1,HA,HC,HS,HW,CCST,RHO,XSA,XCAU,CSA,CCAU,ZET,WSA,WCAU,CCAUS
      COMMON ICD
      OPEN(UNIT=20,DEVICE='DSK',ACCESS='SEQIN',FILE='SWSD')
      DATA WA,WC,WS,WW,WSA,WCAU/17.03,44.01,34.08,18.02,60.05,40/
      RHO = 1
C STATEMENT 1 READS THE OPTION NUMBER AND CONCENTRATIONS OF RCOOH AND
C NAOH IN WT% IN THE LIQUID. THREE OPTIONS ARE PROGRAMED AS FOLLOWS.
C       OPTION NO.        EQUIL. DATA CALC. AT
C          1          CONSTANT TEMPERATURE FROM LIQUID COMPN.
C          2          CONSTANT PRESSURE FROM LIQUID COMPN.
C          3          CONSTANT PRESSURE FROM VAPOR COMPN.
1       READ(20,1001) NOOPT,XSA,XCAUO
C STATEMENT 2 READS TEMPERATURE, DEG. C; PRESSURE, PSIA; PH; AND WT%
C RESPECTIVELY OF NH3, CO2, H2S, AND H2O IN THE STREAM. FOR OPTIONS 1 AND
C 2 THIS WILL BE A LIQUID COMPOSITION; FOR OPTION 3 IT WILL BE A VAPOR
C COMPOSITION. FOR OPTIONS 2&3 THE TEMPERATURE GIVEN IS USED AS A STARTING
C POINT FOR THE ITERATIVE CALCULATION OF AN ISOBARIC TEMPERATURE. STEAM
C REQUIREMENTS AT A GIVEN CONDENSER TEMPERATURE AND PRESSURE CAN BE
C CALCULATED IN OPTION 3 BY SPECIFYING THE VAPOR COMPOSITION ON A WATER-
C FREE BASIS AND BY ENTERING A VALUE OF ZERO FOR THE WATER CONCENTRATION.
C FOR OPTION 1 THE PRESSURE IS NOT USED. IF A POSITIVE VALUE OF PH IS
C GIVEN, THE PROGRAM CALCULATES THE AMOUNT OF CAUSTIC NECESSARY TO OBTAIN
C THE SPECIFIED PH; THEN IT CALCULATES THE VAPOR-LIQUID EQUILIBRIA OF THE
C COMPONENTS AT THIS PH. IF A NEGATIVE VALUE FOR PH IS SPECIFIED THE
C COMPUTER IGNORES THE VALUE AND CALCULATES A PH BASED ON THE LIQUID
C COMPOSITION DETERMINED IN THE EQUILIBRIUM CALCULATION. THESE PH'S
C CORRESPOND TO VALUES AT THE TEMPERATURE OF THE EQUILIBRIUM CALCULATION.
C PH'S AT ROOM TEMPERATURE CAN BE CALCULATED BY DOING AN EQUILIBRIUM
C CALCULATION AT ROOM TEMPERATURE USING THE LIQUID COMPOSITION FROM A
C POINT AT HIGHER TEMPERATURE.
```

(continued)

TABLE 5 (continued)

Reproduced from best available copy.

```
2       READ(20,1000) TC,PSI,PHO,XA,XC,XS,XW
        IF(XW) 10,10,20
10      ICD = 1
        GO TO 30
20      ICD = 0
30      XCAU = XCAUO
C CONVERT TO ABSOLUTE TEMPERATURES IN DEG. K AND DEG. R.
        TK = TC+273.15
        TR = TK*1.8
C A SMALL VALUE IS ADDED TO THE COMPOSITIONS IN ORDER TO AVOID CALCULATION
C PROBLEMS AT ZERO CONCENTRATIONS.
        XA = XA+1E-12
        XC = XC+1E-12
        XS = XS+1E-12
        XW = XW+1E-12
C NEGATIVE AMMONIA CONCENTRATION SIGNALS NEW OPTION, RCOOH, OR CAUSTIC
C DATA.
        IF(XA) 1,200,200
200     GO TO (300,400,500),NOOPT
C OPTION 1 CALCULATES PRESSURE AND VAPOR COMPOSITION FROM SPECIFIED
C TEMPERATURE AND LIQUID COMPOSITION. SUBROUTINE FUNCTIONS ARE LISTED WITH
C THE SUBROUTINES
300     CALL CFX
        PH = 7
        HIO = 1
        CALL PHST
        CALL KREAC
        ELI = CA
C ITERATION LOOP TO CALCULATE EITHER EQUILIBRIUM PH OR EQUILIBRIA AT
C SPECIFIED PH.
        DO 310 IC = 1,100
        CALL SPECL
        CALL NPH
        IF(PHO) 305,305,302
302     CCAU = (CCAU+HT)/2
        IF(IC-10) 310,310,330
C TEST FOR PH CONVERGENCE
305     IF(ABS(HT/TOL)-.0001) 330,330,310
310     CONTINUE
320     WRITE(5,1010)
330     CALL PRESY
C EQUILIBRIA CALCULATED; TRANSFER TO PRINT OUT OF RESULTS.
        GO TO 900
C OPTION 2 CALCULATES TEMPERATURE AND VAPOR COMPOSITION FROM SPECIFIED
C PRESSURE AND LIQUID COMPOSITION.
400     CALL CFX
        P = PSI
        ELI = CA
        PH = 7
        HIO = 1
C FIRST DO LOOP ITERATES TO DETERMINE TEMPERATURE.
```

(continued)

TABLE 5 (continued)

```
      DO 440 IE=1,100
      CALL PHST
      CALL KREAC
C SECOND DO LOOP ITERATES TO FIND EQUIL. PH AT ITERATION TEMPERATURE.
      DO 410 IC = 1,100
      CALL SPECL
      CALL NPH
      IF(PHO) 405,405,402
402   CCAU = (HT+CCAU)/2
      IF(IC-10) 410,410,430
C TEST FOR PH CONVERGENCE
405   IF(ABS(HT/TOL)-.0001) 430,430,410
410   CONTINUE
420   WRITE(5,1010)
430   CALL PRESY
      CALL NTEMP
C TEST FOR PRESSURE CONVERGENCE.
      IF(ABS(PSI/P-1)-.001) 460,460,440
440   CONTINUE
      WRITE(5,1011)
C EQUILIBRIA CALCULATED; TRANSFERS TO PRINT OUT OF RESULTS.
460   GO TO 900
C OPTION 3 CALCULATES TEMPERATURE AND LIQUID COMPOSITION FROM SPECIFIED
C PRESSURE, VAPOR COMPOSITION, PLUS WT% OF RCOOH AND CAUSTIC IN LIQUID.
500   CALL YFX
      P = PSI
      CSA = 10*XSA*RHO/WSA
      CCAU = 10*XCAU*RHO/WCAU
      ELI = 0
      CC = 0
      CA = 0
      CS = 0
      CAS = 0
      PH = 8
      HIO = 1
C FIRST DO LOOP ITERATES TO DETERMINE TEMPERATURE.
      DO 530 IE = 1,100
      CALL PHST
C SECOND DO LOOP ITERATES TO FIND EQUIL. PH AT ITERATION TEMPERATURE.
      DO 510 IC=1,100
      CALL KREAC
      CALL SPECV
      CALL NPH
      IF(PHO) 505,505,502
502   CCAU = (CCAU+HT)/2
      IF(IC-10) 510,520,520
C TEST FOR PH CONVERGENCE.
505   IF(ABS(HT/TOL)-.0001) 520,520,510
510   CONTINUE
515   WRITE(5,1010)
520   CALL NTEMP
```

(continued)

TABLE 5. (continued)

```
C TEST FOR PESSURE CONVERGENCE.
      IF(ABS(PSI/P-1)-.001) 550,550,530
530   CONTINUE
      WRITE(5,1011)
C EQUILIBRIA CALCULATED; TRANSFER TO PRINT OUT OF RESULTS.
550   GO TO 900
C COMPOSITION DATA IN THE LIQUID PHASE ARE USED IN THE PROGRAM IN TERMS
C OF MOLES OF COMPOUND PER KILOGRAM OF SOLUTION. THE VAPOR PHSAE IS IN TERMS
C OF MOLE FRACTION. THE NEXT TEN STATEMENTS CONVERT THESE BACK TO WEIGHT
C PERCENT. THE ORIGINAL CONVERSION OF THE INPUT DATA TO MOLES PER KILOGRAM
C AND VAPOR MOLE FRACTION IS DONE IN SUBROUTINES CFX, YFX, AND FOR OPTION
C 3 PARTLY IN THE MAIN PROGRAM.
900   XA = 100*CA*WA/(1000*RHO)
      XC = 100*CC*WC/(1000*RHO)
      XS = 100*CS*WS/(1000*RHO)
      XCAU = 100*CCAU*WCAU/(1000*RHO)
      XW = 100-XA-XC-XS-XSA-XCAU
      YT = YA*WA+YC*WC+YS*WS+YW*WW
      YA = 100*YA*WA/YT
      YC = 100*YC*WC/YT
      YS = 100*YS*WS/YT
      YW = 100*YW*WW/YT
      XMT = XA/WA+XC/WC+XS/WS+XCAU/WCAU+XW/WW+XSA/WSA
      XMT = 100/XMT
      XMA = XA*XMT/WA
      XMC = XC*XMT/WC
      XMS = XS*XMT/WS
      XMCAU = XCAU*XMT/WCAU
      XMW = XW*XMT/WW
      XMSA = XSA*XMT/WSA
      YMT = YA/WA+YC/WC+YS/WS+YW/WW
      YMT = 100/YMT
      YMA = YA*YMT/WA
      YMC = YC*YMT/WC
      YMS = YS*YMT/WS
      YMW = YW*YMT/WW
      TF = TC*1.8+32
      PKPA = P*6.895
      ATM = P/14.696
C OUTPUT FROM THE FOLLOWING STATEMENTS IS MORE OR LESS SELF EXPLANATORY
C IN THE FORMAT STATEMENTS.
      WRITE(5,1030) TC,TF,TK,TR,P,ATM,PKPA,PH
      WRITE(5,1020)
      EK = YMA/XMA
      WRITE(5,1040) XA,YA,XMA,YMA,EK
      EK = YMC/XMC
      WRITE(5,1050) XC,YC,XMC,YMC,EK
      EK = YMS/XMS
      WRITE(5,1060) XS,YS,XMS,YMS,EK
      EK = YMW/XMW
      WRITE(5,1070) XW,YW,XMW,YMW,EK
```

(continued)

TABLE 5 (continued)

```
      WRITE(5,1072) XSA,XMSA
      WRITE(5,1074) XCAU,XMCAU
      XTOT = XA+XC+XS+XW+XSA+XCAU
      XMTOT = XMA+XMC+XMS+XMW+XMSA+XMCAU
      YTOT = YA+YC+YS+YW
      YMTOT = YMA+YMC+YMS+YMW
      WRITE(5,1075) XTOT,YTOT,XMTOT,YMTOT
      GO TO 2
1000  FORMAT(10E)
1001  FORMAT(I,2E)
1010  FORMAT(' PH DID NOT CONVERGE IN 100 CYCLES')
1011  FORMAT(' TEMPERATURE DID NOT CONVERGE IN 100 CYCLES')
1020  FORMAT(
     1'                          WEIGHT PERCENT       MOLE PERCENT'/
     2' COMPONENT              LIQUID      VAPOR    LIQUID      VAPOR    K
     3-VALUE')
1030  FORMAT(//
     1' TEMPERATURE',F8.2,' C,   ',F8.2,' F,  ',F8.2,' K,',F8.2,' R'/
     2' PRESSURE  ',F8.2,' PSIA,',F8.3,' ATM,',F9.2,' K-PASCALS'/
     3' PH',8X,F8.3//)
1040  FORMAT(' AMMONIA          ',5F10.5)
1050  FORMAT(' CARBON DIOXIDE   ',5F10.5)
1060  FORMAT(' HYDROGEN SULFIDE',5F10.5)
1070  FORMAT(' WATER            ',5F10.5)
1072  FORMAT(' CARBOXYLIC ACID ',F10.5,10X,F10.5)
1074  FORMAT(' SODIUM HYDROXIDE',F10.5,10X,F10.5)
1075  FORMAT(' TOTAL            ',5F10.5)
1080  FORMAT(X,F4.0,3F7.3,7F6.2,9F6.3,F6.2)
      END
```

TABLE 6. SUBROUTINE KREAC

```
      SUBROUTINE KREAC
C THIS SUBROUTINE CALCULATES CHEMICAL EQUILIBRIUM CONSTANTS AS FOLLOWS.
C       SYMBOL              EQUILIBRIUM
C        EKS          H2S FIRST IONIZATION
C        EKCAO        CO2 FIRST IONIZATION AT ZERO IONIC STRENGTH
C        EKCB         CO2 SECOND IONIZATION
C        EKA          NH3 PLUS PROTON GOING TO AMMONIUM ION
C        EKW          WATER DISSOCIATION
C        EKCC         BICARBONATE PLUS AMMONIA GOING TO CARBAMATE
C        EKSB         H2S SECOND IONIZATION
C        EKSA         RCOOH IONIZATION
C THE EFFECT OF IONIC STRENGTH ON EKCAO IS CALCULATED BY THE CALLING PROGRAM.
      COMMON IC,IK,IR,PSI,P,XA,XC,XS,XW,CA,CC,CS,CAS,CCS,CSS,
     1YA,YC,YS,YW,WA,WC,WS,WW,PHO,PH,TOL,MT,DPH,PHA,PHB,AL,BT,GA,
     2DE,ST,HP,SD,EPS,EKS,EKCA,EKCAO,EKCB,EKA,EKW,EKCC,EKSB,EKSA,HTO,
     3ELI,HA,HC,HS,HW,CCST,RHO,XSA,XCAU,CSA,CCAU,ZET,WSA,WCAU,CCAUS
      EKS = EXP(-293.88+683858/TR-6.27125E8/(TR*TR)+2.5551E11/(TR**3)
     1-3.91757E13/(TR**4)+.427*CC)
      EKCAO = EXP(-241.79+536256/TR-4.8123E8/(TR*TR)+1.94E11/(TR**3)
     1-2.96445E13/(TR**4)-.278*CS)
      EKCB = EXP(-295.6+655893/TR-5.9667E8/(TR*TR)+2.4249E11/(TR**3)
     1-3.7192E13/(TR**4))
      EKA = EXP(1.587+11160/TR)
      EKW = EXP(39.5554-177822/TR+1.843E8/(TR*TR)-.8541E11/(TR**3)
     1+1.4292E13/(TR**4))
      EKCC = EXP(-5.40+1925*1.8/TR)
      EKSB = EXP(-657.965+1649360/TR-15.8964E8/(TR*TR)+6.72472E11/(TR
     1**3)-10.6043E13/(TR**4))
      EKSA = EXP(-11.28)
      RETURN
      END
```

TABLE 7. SUBROUTINE HENRY

```
      SUBROUTINE HENRY
C THIS SUBROUTINE CALCULATES HENRY'S CONSTANTS FOR NH3,CO2, H2S, AND H2O
C RESPECTIVELY AS HA, HC, HS, AND HW. HA OF AMMONIA IS DEPENDENT ON THE
C CONCENTRATIONS OF SPECIES NH3, CO2, AND H2S RESPECTIVELY BY THE SYMBOLS
C CAS, CC, AND CS. HS OF H2S IS DEPENDENT ON CAS AND CC. HW FOR WATER IS
C THE VAPOR PRESSURE OF WATER.
      COMMON TC,TK,TR,PSI,P,XA,XC,XS,XW,CA,CC,CS,CAS,CCS,CSS,
     1YA,YC,YS,YW,WA,WC,WS,WW,PHO,PH,TOL,HT,DPH,PHA,PHB,AL,BT,GA,
     2DE,SI,HP,SD,EPS,EKS,EKCA,EKCAO,EKCB,EKA,EKW,EKCC,EKSB,EKSA,HTO,
     3ELI,HA,HC,HS,HW,CCST,RHO,XSA,XCAU,CSA,CCAU,ZET,WSA,WCAU,CCAUS
      TK = TR/1.8
      HA = EXP(178.339-15517.91/TR-25.6767*ALOG(TR)
     1+.01966*TR+(131.4/TR-.1682)*CAS
     1+.06*(2*CC+CS))
      HC = EXP(18.33-24895.1/TR+.223996E8/(TR*TR)-.090918E11/(TR**3)
     1+.12601E13/(TR**4))
      HS = EXP(100.684-24.6254E4/TR+2.39029E8/(TR*TR)-1.01898E11/(TR
     1**3)+1.59734E13/(TR**4)-.05*CAS+(.965-486/TR)*CC)
      HW = EXP(14.466-6996.6/(TR-77.67))
      RETURN
      END
```

TABLE 8. SUBROUTINE YFX

```
      SUBROUTINE YFX
C THIS SUBROUTINE CONVERTS COMPOSITIONS IN WT% TO VAPOR CONCENTRATIONS
C IN MOLE FRACTION. VAPOR COMPOSITIONS FOR NH3,CO2, H2S, AND WATER RESPECTIVE
C ARE GIVEN BY THE SYMBOLS YA, YC, YS, AND YW.
      COMMON TC,TK,TR,PSI,P,XA,XC,XS,XW,CA,CC,CS,CAS,CCS,CSS,
     1YA,YC,YS,YW,WA,WC,WS,WW,PHO,PH,TOL,HT,DPH,PHA,PHB,AL,BT,GA,
     2DE,SI,HP,SD,EPS,EKS,EKCA,EKCAO,EKCB,EKA,EKW,EKCC,EKSB,EKSA,HTO,
     3ELI,HA,HC,HS,HW,CCST,RHO,XSA,XCAU,CSA,CCAU,ZET,WSA,WCAU,CCAUS
      XT = XA/WA+XC/WC+XS/WS+XW/WW
      YA = XA/(WA*XT)
      YC = XC/(WC*XT)
      YS = XS/(WS*XT)
      YW = XW/(WW*XT)
      CA = 1
      RETURN
      END
```

TABLE 9. SUBROUTINE CFX

```
      SUBROUTINE CFX
C THIS SUBROUTINE CONVERTS COMPOSITIONS IN WTX TO LIQUID CONCENTRATIONS
C IN MOLES PER KG OF SOLUTION. LIQUID COMPOSITIONS FOR NH3, CO2, H2S, RCOOH,
C AND CAUSTIC RESPECTIVELY ARE GIVEN BY THE SYMBOLS CA, CC, CS, CSA, AND CCAU
      COMMON TC,TK,TR,PSI,P,XA,XC,XS,XW,CA,CC,CS,CAS,CCS,CSS,
     1YA,YC,YS,YW,WA,WC,WS,WW,PHO,PH,TOL,HT,DPH,PHA,PHB,AL,BT,GA,
     2DE,SI,HP,SD,EPS,EKS,EKCA,EKCAO,EKCB,EKA,EKW,EKCC,EKSB,EKSA,HTO,
     3ELI,HA,HC,HS,HW,CCST,RHO,XSA,XCAU,CSA,CCAU,ZET,WSA,WCAU,CCAUS
      F = 1000*RHO/(XA+XC+XS+XW+XSA+XCAU)
      CA = XA*F/WA
      CC = XC*F/WC
      CS = XS*F/WS
      CSA = XSA*F/WSA
      CCAU = XCAU*F/WCAU
      RETURN
      END
```

TABLE 10. PHST

```
      SUBROUTINE PHST
C THIS SUBROUTINE INITIALIZES PARAMETER VALUES FOR ITERATIVE CALCULATION
C OF PH. THIS SUBROUTINE DETERMINES THE VALUE OF THE TOLERANCE TOL TO BE USED
C IN TESTING FOR PH CONVERGENCE, AND INITIALIZES PH AND OTHER PARAMETERS FOR
C THE ITERATION
      COMMON TC,TK,TR,PSI,P,XA,XC,XS,XW,CA,CC,CS,CAS,CCS,CSS,
     1YA,YC,YS,YW,WA,WC,WS,WW,PHO,PH,TOL,HT,DPH,PHA,PHB,AL,BT,GA,
     2DE,SI,HP,SD,EPS,EKS,EKCA,EKCAO,EKCB,EKA,EKW,EKCC,EKSB,EKSA,HTO,
     3ELI,HA,HC,HS,HW,CCST,RHO,XSA,XCAU,CSA,CCAU,ZET,WSA,WCAU,CCAUS
      IF(PHO) 40,30,30
30    PH = PHO
40    PHA = 0
      PHB = 14
      HTA = -CA
      HTB = 2*CC+CS
      IF(HTB+HTA) 50,50,60
50    TOL = -HTA
      GO TO 70
60    TOL = HTB
70    AL = 0
      TOL = TOL+1E-4
      DPH = 1
      EPS = 0
      HTO = 1
      RETURN
      END
```

TABLE 11. SUBROUTINE SPECV

```
      SUBROUTINE SPECV
C THIS SUBROUTINE CALCULATES EQUILIBRIUM SPECIES CONCENTRATIONS IN THE
C LIQUID PHASE FROM A SPECIFIED VAPOR COMPOSITION, TEMPERATURE, AND AN
C ASSUMED PH. SPECIES CONCENTRATIONS IN THE LIQUID ARE GIVEN BY THE FOLLOWING
C SYMBOLS.
C       SYMBOL          SPECIES
C        CAS             NH3
C        CCS             CO2
C        CSS             H2S
C        AL              HCO3-
C        BT              CO3--
C        DE              NH4+
C        EPS             CARBAMATE ION
C        GA              HS-
C        SD              S--
C        SI              OH-
C        ZET             RCOO-
C        CCAUS           NA+
C THIS CALCULATION IS PERFORMED AT AN ASSUMED PH SO THAT SPECIES CONCENTRATIO
C CAN BE SOLVED FROM DIRECT ALGEBRAIC EQUATIONS. SOME ITERATION IS REQUIRED
C BECAUSE OF THE EFFECT OF IONIC STRENGTH ON THE FIRST IONIZATION OF CO2
C AND THE EFFECT OF SPECIES CONCENTRATIONS ON THE VOLATILITY OF NH3 AND H2S.
C ELI = IONIC STRENGTH.
      COMMON TC,TK,TR,PSI,P,XA,XC,XS,XW,CA,CC,CS,CAS,CCS,CSS,
     1YA,YC,YS,YW,HA,HC,HS,HW,PHO,PH,TOL,HT,DPH,PHA,PHB,AL,BT,GA,
     2DE,SI,HP,SD,EPS,EKS,EKCA,EKCAO,EKCB,EKA,EKW,EKCC,EKSB,EKSA,HTO,
     3ELI,HA,HC,HS,HW,CCST,RHO,XSA,XCAU,CSA,CCAU,ZET,WSA,WCAU,CCAUS
      COMMON ICU
      CALL HENRY
      XW = .9
      PW = 1E-19
      PA = 0
      PC = 0
      PS = 0
      EKCA = EKCAO
      DO 30 I=1,100
      EKAP = EKCA
      EKCA = EKCAO*EXP((-1.32+1558.8/TR)*ELI**.4)
      EKCA = SQRT(EKAP*EKCA)
      PWO = PW
      PAO = PA
      PCO = PC
      PSO = PS
      PW = HW*XW
      IF(ICD) 6,6,2
2     P = PSI
      IF(PSI-PW) 3,3,5
3     WRITE(5,4)
4     FORMAT(' WATER PARTIAL PRESSURE IN CONDENSER GREATER THAN
     1 TOTAL PRESSURE')
      YW = 1
      YA = 1E-12*YA
      YC = 1E-12*YC
      YS = 1E-12*YS
```

(continued)

TABLE 11. (continued)

```
          P = PW
          ICO = 0
          GO TO 6
 5        YW = PW/PSI
          YTOT = (1-YW)/(YA+YC+YS)
          YA = YA*YTOT
          YC = YC*YTOT
          YS = YS*YTOT
          PA = PSI*YA
          PC = PSI*YC
          PS = PSI*YS
          GO TO 7
 6        PA = (YA*PW/YW+PA)/2
          PC = (YC*PW/YW+PC)/2
          PS = (YS*PW/YW+PS)/2
          PBA = P
          P = PW+PA+PC+PS
 7        CAS = PA/HA
          CCS = PC/HC
          CSS = PS/HS
          HP = EXP(-2.30259*PH)
          AL = EKCA*CCS/HP
          BT = EKCB*AL/HP
          DE = EKA*HP*CAS
          EPS = EKCC*CAS*AL
          GA = EKS*CSS/HP
          SD = EKSH*GA/HP
          SI = EKW/HP-CCAU
          ZET = EKSA*CSA/(HP+EKSA)
          CCAUS = CCAU-SI
          CA = CAS+DE+EPS
          CC = CCS+AL+BT+EPS
          CS = CSS+GA+SD
          ELI = ((AL+4*BT+DE+EPS+GA+4*SD+SI+HP+ZET+CCAUS+CCAU)/2+ELI)/2
          TNW = (1000*RHO-CA*WA-CC*WC-CS*WS-CSA*WSA-CCAU*WCAU)/WW
     1-AL+EPS-SI
          TNM = CA+CC+CS+BT-DE+GA+SD+SI+TNW+ZET+2*CCAU+CSA
          XWO = XW
          XW = TNW/TNM
          XW = (XW+XWO)/2
 8        IF(XW) 80,80,9
 80       XW = XW+.1
          GO TO 8
C TEST FOR ITERATION CONVERGENCE
 9        IF(ABS(PW/PWO-1.)-.001) 10,10,30
 10       IF(ABS(PA/PAO-1.)-.001) 15,15,30
 15       IF(ABS(PC/PCO-1.)-.001) 20,20,30
 20       IF(ABS(PS/PSO-1.)-.001) 50,50,30
 30       CONTINUE
 35       WRITE(5,40)
 40       FORMAT(' DIDNT CALCULATE LIQUID IN 100 CYCLES')
 50       RETURN
          END
```

TABLE 12. SUBROUTINE NPH

```
      SUBROUTINE NPH
C THIS SUBROUTINE CALCULATES A NEW ESTIMATED PH FROM A PREVIOUS PH.
C CRITERIA USED ARE THE SUM OF IONIC CHARGES TO ELECTRICAL NEUTRALITY, HT;
C AND ANY CHANGES IN SIGN OF HT FROM A PREVIOUS ITERATION.
      COMMON TC,TK,TR,PSI,P,XA,XC,XS,XW,CA,CC,CS,CAS,CCS,CSS,
     1YA,YC,YS,YW,WA,WC,WS,WW,PHO,PH,TOL,HT,DPH,PHA,PHB,AL,BT,GA,
     2DE,SI,HP,SD,EPS,EKS,EKCA,EKCAO,EKCB,EKA,EKW,EKCC,EKSB,EKSA,HTO,
     3ELI,HA,HC,HS,HW,CCST,RHO,XSA,XCAU,CSA,CCAU,ZET,WSA,WCAU,CCAUS
      HT = AL+2*BT+GA-DE+SI-HP+2*SD+EPS+ZET-CCAU
      TOL = 2*CC+CS
      IF(TOL-CA) 60,70,70
60    TOL = CA
70    IF(PHO) 81,81,80
80    HT = HT+CCAU
      GO TO 88
81    IF(HT/DPH) 84,84,82
82    HTO = .5*HTO
84    DPH = -HT*HTO/(ABS(HT)+1E-19)
      PH = PH+DPH
      GO TO (88,88,85),NDOPT
85    REF = HP*(HT+EKA*CAS*HP)
      PH = SQRT(REF/(EKA*CAS))
      PH = -.5*ALOG(PH*HP)/2.30259
88    RETURN
      END
```

TABLE 13. SUBROUTINE SPECL

Reproduced from best available copy.

```
      SUBROUTINE SPECL
C THIS SUBROUTINE CALCULATES EQUILIBRIUM SPECIES CONCENTRATIONS IN THE LIQUID
C PHASE FROM A SPECIFIED LIQUID COMPOSITION, TEMPERATURE, AND AN ASSUMED
C PH. SYMBOLS USED FOR SPECIES CONCENTRATIONS ARE THE SAME AS FOR SPECV.
C ITERATION IS NECESSARY BECAUSE THE CARBAMATE CONCENTRATION CANNOT BE
C SOLVED DIRECTLY, AND BECAUSE EKCA IS DEPENDENT ON IONIC STRENGTH.
      COMMON TC,TK,TR,PSI,P,XA,XC,XS,XW,CA,CC,CS,CAS,CCS,CSS,
     1YA,YC,YS,YW,WA,WC,WS,WW,PHO,PH,TOL,MT,DPH,PHA,PHB,AL,BT,GA,
     2DE,SI,HP,SD,EPS,EKS,EKCA,EKCAO,EKCH,EKA,EKW,EKCC,EKSH,EKSA,MTO,
     3ELI,HA,HC,HS,HW,CCST,RHO,XSA,XCAU,CSA,CCAU,ZET,WSA,WCAU,CCAUS
      HP = EXP(-2.30259*PH)
      AL = CC
      DO 734 IAL = 1,100
      EKCA = EKCAO*EXP((-1.32+1558.8/TR)*ELI**.4)
      CCS = HP*AL/EKCA
      BT = EKCB*AL/HP
      DE = EKA*HP*CA/((1+AL*EKCC)*(1+EKA*HP/(1+AL*EKCC)))
      EPS = AL*EKCC*(CA-DE)/(1+AL*EKCC)
      CCST = CCS+AL+BT+EPS
C TEST FOR ITERATION CONVERGENCE
      IF(ABS(CCST/CC-1)-.0001) 736,736,732
732   IF(CCST-1E-16) 733,733,7340
733   AL = CC/2
      CCS = CC/2
      BT = 1E-19
      DE = EKA*HP*CA/(1+EKA*HP)
      EPS = 1E-19
      GO TO 736
7340  AL = AL*CC/CCST
      GA = CS*EKS/(HP*(1+(1+EKSB/HP)*EKS/HP))
      SD = GA*EKSB/HP
      SI = EKW/HP-CCAU
      ZET = EKSA*CSA/(HP+EKSA)
      CCAUS = CCAU-SI
734   ELI = (AL+4*BT+DE+EPS+GA+4*SD+SI+HP+ZET+CCAUS+CCAU)/2
7341  WRITE(5,735)
735   FORMAT(' CARBAMATE DIDNT CONVERGE IN 100 CYCLES')
736   RETURN
      END
```

TABLE 14. SUBROUTINE PRESY

```
      SUBROUTINE PRESY
C THIS SUBROUTINE CALCULATES EQUILIBRIUM VAPOR COMPOSITION AND PRESSURE
C FROM TEMPERATURE AND CALCULATED SPECIES CONCENTRATIONS OF NH3, CO2, AND H2S
C IN THE LIQUID
      COMMON TC,TK,TR,PSI,P,XA,XC,XS,XW,CA,CC,CS,CAS,CCS,CSS,
     1YA,YC,YS,YW,WA,WC,WS,WW,PHO,PH,TOL,HT,DPH,PHA,PHB,AL,BT,GA,
     2DE,SI,HP,SD,EPS,EKS,EKCA,EKCAO,EKCB,EKA,EKW,EKCC,EKSB,EKSA,HTO,
     3ELI,HA,HC,HS,HW,CCST,RHO,XSA,XCAU,CSA,CCAU,ZET,WSA,WCAU,CCAUS
      CCS = HP*AL/EKCA
      CSS = HP*GA/EKS
      CAS = DE/(EKA*HP)
      CALL HENRY
      PA = CAS*HA
      PC = CCS*HC
      PS = CSS*HS
      TNW = (1000*RHO-CA*WA-CC*WC-CS*WS-CSA*WSA-CCAU*WCAU)/WW
     1-AL+EPS-SI
      TNM = CA+CC+CS+BT-DE+GA+SD+SI+TNW+ZET+2*CCAU+CSA
      PW = TNW*HW/TNM
      P = PA+PC+PS+PW
      YA = PA/P
      YC = PC/P
      YS = PS/P
      YW = PW/P
      RETURN
      END
```

TABLE 15. SUBROUTINE NTEMP

```
      SUBROUTINE NTEMP
C THIS SUBROUTINE ESTIMATES A NEW TEMPERATURE IN AN ITERATIVE CALCULATION
C TO AGREE WITH A SPECIFIED PRESSURE. THE ONLY CRITERION USED IS THE CALCULAT
C PRESSURE OF A PREVIOUS ITERATION VERSUS THE SPECIFIED PRESSURE. AN ASSUMEI
C EFFECTIVE HEAT OF VAPORIZATION OF 9000X1.987 BTU PER POUND MOLE IS USED
C TO ESTIMATE A NEW TEMPERATURE.
      COMMON TC,TK,TR,PSI,P,XA,XC,XS,XW,CA,CC,CS,CAS,CCS,CSS,
     1YA,YC,YS,YW,WA,WC,WS,WW,PHO,PH,TOL,HT,DPH,PHA,PHB,AL,BT,GA,
     2DE,SI,HP,SD,EPS,EKS,EKCA,EKCAO,EKCB,EKA,EKW,EKCC,EKSB,EKSA,HTO,
     3ELI,HA,HC,HS,HW,CCST,RHO,XSA,XCAU,CSA,CCAU,ZET,WSA,WCAU,CCAUS
      TR1 = TR
      TR = -ALOG(PSI/P)/9000+1/TR1
      TR = 1/TR
      TC = TR/1.8-273.15
      TK = TR/1.8
      RETURN
      END
```

Subroutine	Table No.	Function of Subroutine
KREC	6	Calculates chemical equilibrium constants from parameters in Tables 3 and 4
HENRY	7	Calculates Henry's constants from parameters in Table 1
YFX	8	Converts vapor compositions in wt % to vapor concentrations in mole fraction
CFX	9	Converts liquid compositions in wt % to liquid concentrations in moles/Kg of solution
PHST	10	Initializes pH iteration parameters
SPECV	11	Calculates pressure and equilibrium species concentrations in the liquid phase from a specified vapor composition, temperature, and asssumed pH
NPH	12	Calculates a new estimated pH from a previous pH
SPECL	13	Calculates equilibrium species concentrations in the liquid phase from a specified liquid composition, temperature, and an assumed pH
PRESY	14	Calculates equilibrium vapor concentrations and pressure from temperature and calculated species concentrations in the liquid
NTEMP	15	Estimates a new temperature in an iterative calculation so that the calculated pressure will agree with a specified pressure

A discussion of each of these subroutines in the order listed above is given in the following text of this report.

KREAC

Equations used in KREAC come from Tables 3 and 4. The symbols used in the subroutine relate to the various chemical reactions in Table 2 as follows.

Fortran Symbol	Chemical Reaction in Table 2
EKS	5
EKCAO	1
EKCB	2
EKA	3
EKW	7
EKCC	4
EKSB	6
EKSA	8

The effect of ionic strength of EKCAO of reaction 1 is not computed in the subroutine because it changes each pH iteration. This effect is therefore computed in subroutine SPECL for each pH iteration cycle where the ionic strength from the previously computed cycle is used for the next iteration.

HENRY

Equations used in HENRY come from Table 1. The symbols used in the subroutine relate to the Henry's constant parameters given in Table 1 as follows.

Fortran Symbol	Henry's Constant for
HA	free NH_3
HC	free CO_2 (or H_2CO_3)
HS	free H_2S
HW	vapor pressure of water

YFX

The conversion of wt.% in the vapor to mole % in the vapor from subroutine YFX is fairly straight forward. The fortran symbols and associated molecular weights entered by means of a data statement at the beginning of the main program are as follows.

Component	Symbol	Molecular Weight
NH_3	WA	17.03
CO_2	WC	44.01
H_2S	WS	34.08
H_2O	WW	18.02
RCOOH	WSA	60.05
NaOH	WCAU	40

CFX

Subroutine CFX is similar to YFX except that the concentrations in wt. % are converted to liquid concentrations in moles/Kg of solution. To do this, the sum of all wt.% given as input to the program are summed and divided into 1000 x RHO to obtain the normalizing factor. A value of RHO = 1 has to be used or the concentrations will not come out in moles/Kg of solution. This assignment is made in the main program as the first executable statement. The number of moles of each component is then computed from the normalizing factor times its concentration on a weight basis divided by its molecular weight.

PHST

Subroutine PHST initializes parameters used in the pH iteration procedure. If a positive PHO (for pH) is specified to the subroutine, then the subroutine assigns PH = PHO and the other parameters have no effect. If a negative PHO is specified then it means that the program must compute the pH.

In this case, it assigns the limits over which the pH can be varied which are from 0 to 14 and assigns a tolerance to be used by subroutine NPH to test for convergence. The tolerance variable is assigned to either the sum of acid gas concentrations if they are in excess or to the NH_3 concentration if it is in excess. Carbon dioxide reacts with two moles of NH_3, so its concentration is multiplied by two in computing the acid gas concentration. If the tolerance assigned by this method is less than 1×10^{-4} then a tolerance of 1×10^{-4} moles/Kg of solution is assigned. The variables DPH and HTO are iteration parameters used by NPH. For their use, see subroutine NPH.

SPECV

Subroutine SPECV is the main subroutine used in option 3 to calculate temperature and liquid composition from specified pressure, vapor composition, plus RCOOH and/or caustic in the liquid. The steps of this subroutine are not too obvious, so details of the calculation procedure will be discussed here. Temperature iteration and pH iteration are done outside of the subroutine, so the subroutine calculates pressure and liquid composition from temperature, pH, and a specified vapor composition. This is d ne by first estimating the partial pressure of water in the vapor phase using the vapor pressure of water and Raoult's law as follows.

$$PW = (HW) \times (XW) \qquad (29)$$

where PW = water partial pressure
HW = vapor pressure of water
XW = mole fraction water in liquid phase; initially assumed to be 1.0

The partial pressures of the other components are then calculated from the mole ratio of the components over water times the partial pressure of water.

$$(PA, PC, \text{ and } PS) = \frac{(YA, YC, \text{ or } YS)}{(YW)} \times (PW) \qquad (30)$$

where PA, PC, and PS = partial pressures of NH_3, CO_2, and H_2S, respectively

YA, YC, or YS = vapor mole fractions
YW = water mole fraction
PW = water partial pressure

The total pressure P is then calculated as the sum of the partial pressures; and the concentrations of free NH_3 (CAS), CO_2 (CSS), and H_2S (CSS) are calculated from their partial pressure divided by the Henry's constant of each component. These Henry's constants depend on the composition of the liquid phase so this computation involves an iterative procedure where Henry's constants computed from the liquid composition. This procedure could diverge instead of converge, so each new partial pressure is assumed to be the average of the new computed partial pressure and the old computed partial pressure. This technique requires a minimum of ten iterations to achieve an accuracy of $\pm$.0.1%; so it uses more computer time in order to avoid possibility of

diverging instead of converging. A maximum of 100 cycles is specified in the subroutine for convergence; if this number is specified in the subroutine for convergence; if this number is exceeded, the subroutine writes to unit 5 a warning signal that 100 cycles are exceeded. If this occurs, one may want to give the old partial pressure more weight than the new one so as to improve convergence.

Once the concentrations of free NH_3, CO_2, and H_2S in the liquid have been calculated for each iteration cycle, then the concentrations of all species concentrations in the liquid phase can be computed according to the chemical equilibria summarized in Table 2. Symbols used by the subroutine for each species present are summarized as comment statements at the beginning of the subroutine in Table 11. Once these concentrations have been computed, then the mole fraction of water can be recomputed and then the iteration cycle is repeated. Iterations are continued until the new computed partial pressure of each component equals the old computed partial pressure within a tolerance of $\pm$ 0.1%. In each iteration cycle, the subroutine allows for any RCOOH or caustic specified to be in the liquid phase as input data to the subroutine.

NPH

Subroutine NPH estimates new pH values based on information gained from previous pH iterations. This subroutine uses the requirement of electrical neutrality as the determining equation for either increasing or decreasing the pH. The equation for electrical neutrality can be written as follows.

$$\sum_i C_i Z_i = 0$$

where C_i = concentration of component i in moles/Kg of solution

Z_i = electronic charge

In general, for a randomly selected input pH, the electrical neutrality summation will not equal zero. In this subroutine, this summation is represented by the symbol HT. In order to bring to zero, the step length for a new pH value is computed from the following equation:

$$\Delta pH = C,k) \times (HT)/|HT| \qquad (32)$$

where pH = computed pH increment, DPH
k = a proportionality constant, HTO
HT = electrical neutrality summation
|HT| = absolute value of HT

If HT changes sign compared to a previous iteration, then the proportionality constant k is increased by a factor of two, and the iteration is continued. By this procedure, the pH increments are only determined by the algebraic sign of HT compared with previous iterations. Thus, when HT changes sign, then the increments are reduced by a factor of two. DPH and HTP are intially set to unity by subroutine PHST. This convergence method is slow, but

dependable. Other faster methods could probably be devised to speed up this calculation.

SPECL

Subroutine SPECL is similar to SPECV in that the pH, temperature, and composition of one of the phases is given and the pressure and composition of the other phase is calculated. In the case of SPECL, the total amounts of NH_3, CO_2, H_2S, H_2O, RCOOH, and caustic in the liquid phase are given; and the composition of the vapor phase is calculated.

This subroutine is used for both options 1 and 2 of the main program. The method of computing the concentrations of each individual species in the liquid requires a knowledge of the chemical equilibrium constants which in turn are dependent on the concentrations of the individual species present. Thus, an iterative calculation procedure is required where the ionic strength ELI is initially set to equal the total NH_3 concentration CA in the main program. Subsequent iterations then give better values for the ionic strength. The calculation method used in this subroutine is based on the calculation method discussed in the previous section of this report on the SWEQ model; equations 7 to 22. Because of H_2NCOO^- formation, equations 16 and 17 are not used to solve for α and β; instead α is used as an iteration parameter along with ionic strength. Initially α (Fortran symbol AL) is assumed to be the total CO_2 concentration in the liquid; equations 14 and 15 are then used to calculate the concentration of free CO_2 (CSS) and of H_2NCOO^- ions (BT). These are also listed as equations 1 and 2 in Table 2. The equilibrium NH_4^+ concentration in solution is obtained by simultaneously solving equations 3 and 4 in Table 2 by algebraic methods to obtain the equations for NH_4^+ concentration (DE) and H_2NCOO^- concentration (EPS) used in this subroutine. Iteration is continued until the sum of all CO_2 species equals the amount of CO_2 in the liquid from the starting composition. If the sum of the species concentrations is higher or lower than the starting composition, then AL is proportionately changed by multiplying the old AL by the ratio of starting composition over the sum of the species concentration as follows.

$$AL_{new} = (AL_{old}) \frac{(CC)}{(CCST)} \qquad (33)$$

CC = CO_2 starting concentration

CCST = sum of CO_2 species concentrations

After this calculation, the concentrations of (HS^-) and ($S^=$) ions are calculated using equations similar to equations 16 and 17 in the section on the SWEQ model. The actual equations involved are equations 5 and 6 in Table 2. These can be solved to give the following:

$$\gamma = \frac{K_5 M_5}{\left[(H^+) + k_5 + k_5 k_6/(H^+)\right]} \qquad (34)$$

$$\psi = \frac{k_5 k_6 M_5/(H^+)}{\left[(H^+) \times k_5 + k_5 k_6/(H^+)\right]} \quad \frac{\gamma k_6}{(H^+)} \qquad (35)$$

In the subroutine, these have the following symbols:

	Fortran Symbol
γ	GA
ψ	SD
k_5	EKS
k_6	EKSB
M_5	CS
H^+	HP

After this calculation, the only species left are from RCOOH and from water dissociation; these are calculated from equations 7 and 8 in Table 2 where SI represents the extent of water dissociation and AET represents the extent of RCOOH dissociation. From the calculated species concentrations, the ionic strength can be calculated and iteration is then continued until the sum of CO_2 species equals the CO_2 in the starting composition within $\pm$ 0.01%. When this test is satisfied, the subroutine returns to the main program.

PRESY

This subroutine computes the partial pressure of NH_3, CO_2, H_2S, and water from equations 4, 5, and 6 given in the section on the SWEQ model. To do this, the individual species concentrations of CO_2, H_2S, and NH_3 represented by CCS, CSS, and CAS are computed from equations similar to equation 19 in the section on the SWEQ model. In order to calculate the partial pressure of water, two quantities are first calculated in the subroutine. These are the total number of moles of water, TNW, present in 1 Kg of solution (RHO = 1) and the total moles of all components, TNM, in 1 Kg of solution. TNW is computed from the residual weight left after subtracting the weight of NH_3, CO_2, H_2S, RCOOH, and caustic respectively from the 1000 grams of solution divided by the molecular weight of water. TNM is calculated by summing the moles of all species present including water in 1000 grams of solution. The partial pressure of water is then computed from the vapor pressure of water, HW, times the moles of water over the total moles. The total pressure is then calculated as the sum of the partial pressures, and the vapor mole fraction of each component is calculated from its partial pressure divided by the total pressure.

NTEMP

Subroutine NTEMP is used to estimate the correct temperature for an equilibrium calculation where the total pressure is specified. This occurs

in options 2 and 3. For this purpose a simple equation is used as follows.

$$\ln\left(\frac{P_{specified}}{P_{calculated}}\right) = -9000\left(\frac{1}{T^{o}R_{new}} - \frac{1}{T^{o}R_{old}}\right) \qquad (36)$$

where -9000 corresponds approximately to the heat of vaporization of water.

$$-9000 \cong \frac{\Delta H_{vap}}{1.987} \cong \frac{18{,}000 \text{ Btu/lb mole}}{1.987} \qquad (37)$$

The above equation can be solved for $T^{o}R_{new}$ to give the following:

$$\frac{1}{T^{o}R_{new}} = \frac{1}{T^{o}R_{old}} - \ln\left(\frac{P_{spec}}{P_{calc}}\right) \Big/ 9000 \qquad (38)$$

In the subroutine, these have the following symbols:

$$TR = T^{o}R_{new} \qquad (39)$$

$$PSI = P_{spec.} \qquad (40)$$

$$P = P_{calc.} \qquad (41)$$

$$TRI = T^{o}R_{old} \qquad (42)$$

This subroutine also computes the temperature in ^{o}C from TR before returning to the main program.

Tables 5 to 15 represent a total of ten subroutines used by the main computer program. A large bumber of subroutines are used in order to make it possible to devise various options in the main program. Many options are possible; an attempt was not made to develop programming for each possible option because of the large amount of programming required. Instead, three options were programmed which demonstrate the use of the subroutines. Thus, flow charts for options 1, 2, and 3, given in Figures 2, 3, and 4, primarily involve the use of subroutines with some programming done in between to satisfy the requirements of the option. In option 1, the main iteration is to calculate the pH. When the pH is specified, then the iteration changes slightly to calculate the amount of caustic necessary to achieve the specified pH. This method of calculation occurs in all three options. Distillation options 2 and 3 involve a second iteration loop besides the pH iteration loop. This is necessary to find the correct temperature at a specified pressure. An example of input and output data for the computer program listed in Table 5 is given in Tables 16 and 17.

Table 16 explains the data format to be used in entering data to the computer program. The information in this table must be studied carefully before using the computer program. Table 17 gives an example of computer output from data specified in Table 16. This listing is self explanatory.

The next section of this report gives a numerical example of calculations necessary for an actual design problem and a subsequent section gives data comparisons and evaluations between calculated and measured data.

TABLE 16. INPUT DATA FOR SAMPLE PROBLEM WITH SWEQ COMPUTER PROGRAM

Parameter	Symbol	Value Entered
Option number 3 for calculating liquid composition and temperature from a specified vapor composition and pressure	NDOPT	3
Weight percent carboxylic acid in liquid	XSA	.05
Weight percent caustic in liquid	XCAUO	.05
Temperature, °C (For Option 3 this is used as a starting temperature)	TC	100
Pressure, psia; specified pressure	PSI	20
pH, a positive entry specifies the pH for the calculation. The computer program will adjust the amount of caustic in the liquid independent of the concentration entered above when a positive pH is entered	PHO	8.5
Weight percent concentrations in the vapor phase		
NH_3	XA	.01
CO_2	XC	.01
H_2S	XS	.01
H_2O	XW	100

(continued)

TABLE 16. (continued)

Format for data entry:

3	.05	.05				
NDOPT	XSA	XCAUO				
100	20	8.5	.01	.01	.01	100
TC	PSI	PHO	XA	XC	XS	XW

Additional lines of temp., pressure, etc. can follow

1 1 1 −1 1 1 1 This entry will signal a new option line to follow this one.

NDOPT XSA XCAUO

Then lines of temp., pressure, etc.

TABLE 17. COMPUTER OUTPUT FROM DATA IN TABLE 16 WITH COMPUTER PROGRAM BASED ON THE SWEO MODEL

TEMPERATURE	108.88 C,	227.99 F,	382.03 K,	687.66 R
PRESSURE	20.00 PSIA,	1.361 ATM,	137.90 K-PASCALS	
PH	8.500			

	WEIGHT PERCENT		MOLE PERCENT		
COMPONENT	LIQUID	VAPOR	LIQUID	VAPOR	K-VALUE
AMMONIA	0.00091	0.01000	0.00096	0.01058	11.02807
CARBON DIOXIDE	0.00017	0.01000	0.00007	0.00409	57.78305
HYDROGEN SULFIDE	0.00073	0.01000	0.00039	0.00529	13.62491
WATER	99.93077	99.97001	99.97572	99.98004	1.00004
CARBOXYLIC ACID	0.05000		0.01501		
SODIUM HYDROXIDE	0.01742		0.00785		
TOTAL	100.00000	100.00000	100.00000	100.00000	

SECTION 5

SAMPLE PROBLEM USING THE SWEQ MODEL

Information given in the two prior sections of this report on the SWEQ model and on the computer program based on the SWEQ model can probably be better understood by giving a numerical example which shows the calculations necessary in an actual sour water stripper design case. For this purpose the following sample problem [a] is given.

A refluxed sour water stripper operates at a condenser temperature of 212°F at a pressure of 8.7 psig (23.4 psia). To achieve the desired removal of H_2S and NH_3 from the stripper feed, the overhead gas from the condenser must contain 48 lb/hr of NH_3 and 49.7 lb/hr of H_2S. Determine the amount of water in the exit gas, and the reflux composition.

Gas rates $\quad NH_3 = \dfrac{48 \text{ lb/hr}}{17.03 \text{ lb/lb mole}} = 2.82 \text{ mole/hr}$

$\qquad\qquad H_2S = 49.7/34.08 = 1.46 \text{ mole/hr}$

From Raoult's Law, the partial pressure of water in the vapor phase is:

$$p.p.(H_2O) = (V.P._{H_2O}) \cdot X_{H_2O}$$

Assume that $X_{H_2O} = 0.9$ $\qquad$ At 212°F, $V.P._{H_2O} = 14.7$ psia

$$p.p.(H_2O) = 0.9\ (14.7) = 13.2 \text{ psia}$$

The partial pressure of $(H_2S = NH_3) = 23.4 - 13.2 = 10.2$ psia, therefore the total moles of overhead gas $= (2.82 + 1.46) \times \frac{23.4}{10.2} = 9.82$ moles/hr. Assumed water rate is $9.82 - (2.82 + 1.46) = 5.54$ mole/hr. In summary, the assumed vapor composition is

---

[a] This sample calculation is given through the courtesy of Ron Gantz and co-workers of CONOCO who did the numerical calculations and wrote this sample problem. It has been checked at Brigham Young University and found to be correct.

	lb/hr	mole/hr	mole/fr.	p.p., psia
NH_3	48	2.82	.287	6.72
H_2S	49.7	1.46	.149	3.49
H_2O	99.8	5.54	.564	13.19
		9.82	1.000	23.40

Calculation of the liquid composition in equilibrium with the assumed vapor composition involves simultaneous solution of the appropriate chemical equilibria and phase equilibrium equations. The chemical reactions (Tables 2 to 4) are:

$$H_2O \rightleftarrows H^+ + OH^- \qquad k_{H_2O} = \frac{[H^+][OH^-]}{[H_2O]} \to 1.0$$

$$NH_3 + H^+ \rightleftarrows NH_4^+ \qquad k_{NH_3} = \frac{[NH_4^+]}{[NH_3][H^+]}$$

$$H_2S \rightleftarrows HS^- + H^+ \qquad k_{H_2S} = \frac{[HS^-][H^+]}{[H_2S]}$$

$$HS^- \rightleftarrows S^= + H^+ \qquad k_{HS^-} = \frac{[S^=][H^+]}{[HS^-]}$$

The chemical equilibrium constants are correlated in the general form (Table 4).

$$\ln k_i = A + B/T + C/T^2 + D/T^3 + E/T^4$$

where T is the temperature in ^oR
At 100^{o}C (= 671.7^{o}R),

$$\ln k_{H_2O} = 39.5554 - \frac{177822}{671.7} + \frac{1.843 \cdot 10^8}{(671.7)^2} - \frac{.8541 \cdot 10^{11}}{(671.7)^3} + \frac{1.4292 \cdot 10^{13}}{(671.7)^4}$$

$$k_{H_2O} = 5.054 \cdot 10^{-13}$$

$$\ln k_{NH_3} = 1.587 + 11160/671.7$$

$$k_{NH_3} = 8.032 \cdot 10^7$$

$$\ln k_{H_2S} = -293.88 + \frac{683858}{671.7} - \frac{6.27125 \cdot 10^8}{(671.7)^2} + \frac{2.5551 \cdot 10^{11}}{(671.7)^3} - \frac{3.91757 \cdot 10^{13}}{(671.7)^4}$$

$$k_{H_2S} = 2.805 \cdot 10^{-7}$$

$$\ln k_{HS^-} = -657.965 + \frac{1649360}{671.7} - \frac{15.8964 \cdot 10^8}{(671.7)^2} + \frac{6.72472 \cdot 10^{11}}{(671.7)^3} - \frac{10.6043 \cdot 10^{13}}{(671.7)^4}$$

$$k_{HS^-} = 9.06 \cdot 10^{-13}$$

For phase equilibria, the Henry's Law coefficients from Table 1 are used:

$$\ln (H_{NH_3}) = 178.339 - \frac{15517.91}{(TR)} - 25.6767 \ln (TR) + .01966 \cdot (TR)$$

$$+ \left(\frac{131.4}{TR} - .1682 \right) \cdot C_{AS} + 0.06 \cdot C_S$$

where TR is the temperature in °R

C_{AS} is the free NH_3 concentration (liquid) in gm-moles/Kg

and C_S is the <u>total</u> H_2S concentration (liquid) in gm-moles/Kg

Kg = kilogram

Assume $C_{AS} = C_S = 0$

$$H_{NH_3} = 3.64 \text{ psia/gm-mole/Kg}$$

$$\ln (H_{H_2S}) = 100.684 - \frac{24.6254 \cdot 10^4}{TR} + \frac{2.39029 \cdot 10^8}{TR^2} - \frac{1.01898 \cdot 10^{11}}{TR^3} + \frac{1.59734 \cdot 10^{13}}{TR^4}$$

$$- 0.05 \cancel{C_{AS}}^{\rightarrow 0}$$

$$H_{H_2S} = 442.5 \text{ psia/gm-mole/Kg}$$

From the Henry's Law coefficients for H_2S and NH_3, and the assumed vapor partial pressures, the free H_2S and NH_3 concentrations in the liquid can be calculated:

$$p.p.(NH_3) = H_{NH_3} C_{AS}$$

$$C_{AS} = \frac{p.p.(NH_3)}{H_{NH_3}} = \frac{6.72}{3.64} = 1.85 \text{ gm-mole/Kg}$$

$$C_{SS}(\text{free } H_2S) = \frac{3.49}{442.5} = 7.89 \cdot 10^{-3} \text{ gm-mole/Kg}$$

A pH must now be assumed - use 8.5

A pH must now be assumed - use 8.5

$$pH = -\log_{10}[H^+]$$

$$[H^+] = e^{-2.303 \cdot pH} = 3.15 \cdot 10^{-9}$$

The chemical equilibrium equations can now be solved for the concentrations of all other species in solution:

$$k_{H_2O} = [H^+][OH^-]$$

$$[OH^-] = \frac{k_{H_2O}}{[H^+]} = \frac{5.054 \cdot 10^{-3}}{3.15 \cdot 10^{-9}} = 1.60 \cdot 10^{-4} \text{ gm-ions/Kg}$$

$$k_{NH_3} = \frac{[NH_4^+]}{[NH_3][H^+]}$$

$$[NH_4^+] = [NH_3][H^+]\, k_{NH_3} \qquad \text{Note: } [NH_3] = C_{AS}$$

$$[NH_4^+] = (1.85)(3.15 \cdot 10^{-9})(8.032 \cdot 10^{7}) = 0.468 \text{ gm-ions/Kg}$$

$$k_{H_2S} = \frac{[HS^-][H^+]}{[H_2S]}$$

$$[HS^-] = \frac{k_{H_2S}[H_2S]}{[H^+]} \qquad [H_2S] = C_{SS}$$

$$[HS^-] = \frac{(2.805 \cdot 10^{-7})(7.89 \cdot 10^{-3})}{3.15 \cdot 10^{-9}} = 0.70 \text{ gm-ions/Kg}$$

$$k_{HS^-} = \frac{[S^=][H^+]}{[HS^-]}$$

$$[S^{=}] = \frac{[HS^{-}]k_{HS^{-}}}{[H^{+}]}$$

$$[S^{=}] = \frac{(0.70)(9.06 \cdot 10^{-13})}{3.15 \cdot 10^{-9}} = 2.02 \cdot 10^{-4} \text{ gm-ions/Kg}$$

If the assumed pH and values of C_{AS}, C_{SS} are correct, the solution should be electrically neutral, that is:

$$[H^{+}] + [NH_4^{+}] = [HS^{-}] + 2[S^{=}] + [OH^{-}]$$

$$3.15 \cdot 10^{-9} + 0.468 = 0.68 + 2(2.02 \cdot 10^{-4}) + 1.6 \cdot 10^{-4}$$

$$0.468 \neq 0.68$$

A trial and error procedure for pH, with successive substitution for species concentrations at each pH level, must be used to reach a converged solution.

First, adjust the Henry's Law coefficients for the current values of H_2S and NH_3 concentrations:

$$\ln (H_{NH_3}) = \ln (3.640) + \left(\frac{131.4}{TR} - .1682\right)(C_{AS}) + .06\ C_S$$

where C_S = total $H_2S = C_{SS} + [HS^{-}] + [S^{=}]$

$$= .00789 + 0.68 + 1.96 \cdot 10^{-4} = 0.688 \frac{\text{gm-moles}}{\text{Kg}}$$

$$\ln (H_{NH_3}) = 1.292 + \left(\frac{131.4}{671.7} - .1682\right)(1.85) + .06(.688)$$

$$H_{NH_3} = 3.99 \frac{\text{psia}}{\text{gm-mole/Kg}}$$

$$\ln (H_{H_2S}) = \ln (442.5) = -.05\ C_{AS}$$

$$H_{H_2S} = \frac{403.4 \text{ psia}}{\text{gm-mole/Kg}}$$

Calculate new free H_2S, NH_3 concentrations

$$C_{AS} = \frac{\text{p.p.}(NH_3)}{H_{H_2S}} = \frac{6.72}{3.99} = 1.68 \text{ gm-mole/Kg}$$

$$C_{SS} = \frac{\text{p.p.}(H_2S)}{H_{H_2S}} = \frac{3.49}{403.4} = 8.65 \cdot 10^{-3} \text{ gm-mole/Kg}$$

The total ammonia concentration, C_A, is

$$C_A = C_{AS} + [NH_4^+] = 1.68 + 0.468 = 2.15 \text{ gm-moles/Kg}$$

The total H_2S concentration, C_S, is

$$C_S = C_{SS} + [HS^-] + [S^=] = 8.65 \cdot 10^{-3} + 0.70 + 1.96 \cdot 10^{-4} = .709 \frac{\text{gm-moles}}{\text{Kg}}$$

A new water mole fraction in the liquid should be calculated for use with Raoult's Law to provide a new vapor composition.

A free water concentration, C_{H_2O}

$$C_{H_2O} = [1000 \frac{\text{gm}}{\text{Kg}} - C_S \cdot (\text{mol. wt. } H_2S) - C_A \cdot (\text{mol. wt. } NH_3)] \cdot \frac{1}{\text{mol. wt. } H_2O}$$

$$- [OH^-]$$

$$C_{H_2O} = \frac{[1000 - 0.709(34.08) - 2.15(17.03)]}{18.02} - 1.96 \cdot 10^{-4} \rightarrow 0$$

$$C_{H_2O} = 52.2 \frac{\text{gm-mole}}{\text{Kg}}$$

The free water mole fraction in the liquid is

$$X_{H_2O} = \frac{C_{H_2O}}{\Sigma Ci}$$

$$\Sigma Ci = [NH_3] + [NH_4^+] + [H^+] + [H_2S] + [HS^-] + [S^=] + [H_2O] + [OH^-]$$

$$= 1.68 + .468 + 3.15 \cdot 10^{-9} + 8.65 \cdot 10^{-3} + 0.70 + 1.96 \cdot 10^{-4}$$

$$+ 52.2 + 1.6 \cdot 10^{-4}$$

$$= 55.06$$

$$X_{H_2O} = \frac{52.2}{55.06} = 0.948$$

$$\text{p.p.}(H_2O) = (0.948)(14.7) = 13.9 \text{ psia}$$

$$\text{p.p.}(H_2S + NH_3) = 23.4 - 13.9 = 9.5 \text{ psia}$$

Total moles in the vapor = $4.28 \cdot \frac{23.4}{9.5} = 10.54$

Moles of H_2O vapor = 10.54 = -4.28 = 6.26

The new vapor partial pressures are:

$$p.p.(NH_3) = \frac{2.82}{10.54} \cdot 23.4 = 6.26 \text{ psia}$$

$$p.p.(H_2S) = \frac{1.46}{10.54} \cdot 23.4 = 3.24 \text{ psia}$$

Calculate new free NH_3, H_2S concentrations in the liquid

$$C_{AS} = \frac{p.p.(NH_3)}{H_{NH_3}} = \frac{6.26}{3.99} = 1.57 \frac{\text{gm-moles}}{\text{Kg}}$$

$$C_{SS} = \frac{p.p.(H_2S)}{H_{H_2S}} = \frac{3.24}{403.4} = 8.03 \cdot 10^{-3} \frac{\text{gm-moles}}{\text{Kg}}$$

Using the same pH, calculate new ionic concentrations

$$[OH^-] = \frac{k_{H2O}}{[H^+]} = \frac{5.054 \cdot 10^{-3}}{3.15 \cdot 10\text{-}9} = 1.6 \cdot 10^{-4} \frac{\text{gm-ions}}{\text{Kg}}$$

$$[NH_4^+] = [NH_3][H^+]k_{NH_3}$$

$$= (1.57)(3.15 \cdot 10^{-9})(8.032 \cdot 10^{7}) = 0.397 \frac{\text{gm-ions}}{\text{Kg}}$$

$$[HS^-] = \frac{k_{H_2S}[H_2S]}{[H^+]} = \frac{(2.805 \cdot 10^{-7})(8.03 \cdot 10^{-3})}{3.15 \cdot 10\text{-}9} = .71 \frac{\text{gm-ions}}{\text{Kg}}$$

$$[S^=] = \frac{[HS^-]k_{HS^-}}{[H^+]} = \frac{(0.71)(9.06 \cdot 10^{-13})}{3.15 \cdot 10\text{-}9} = 2.05 \cdot 10^{-4} \frac{\text{gm-ions}}{\text{Kg}}$$

Checking again for neutrality

$$[NH_4^+] + [H^+] = [OH^-] + [HS^-] + 2[S^=]$$

$$0.397 + 3.15 \cdot 10^{-9} = 1.6 \cdot 10^{-4} + 0.71 + 2.05 \cdot 10^{-4} \quad (2)$$

$$0.397 \neq 0.69$$

Since the total electrical charge appears ti be increasing on the negative side, the assumed ph must be incorrect, and nothing further would be gained by converging to final concentrations at this pH.

The major ionic concentrations are $[NH_4^+]$ and $[HS^-]$.

Since $[NH_4^+] = [NH_3][H^+]k_{NH_3}$

and $[HS^-] = \frac{k_{H_2S}[H_2S]}{[H^+]}$,

increasing the value of H^+ would increase NH_4^+ and decrease HS^-. Thus, the correct pH must be lower than the initial assumption of 8.5.

If $[H^+] = 4.15 \cdot 10^{-9}$, and $[NH_3]$, $[H_2S]$ are assumed constant, then

$$[NH_4^+]_{new} = 0.397 \cdot \frac{4.15 \cdot 10^{-9}}{3.15 \cdot 10^{-9}} = 0.523$$

$$(HS^-]_{new} = 0.69 \cdot \frac{3.15 \cdot 10^{-9}}{4.15 \cdot 10^{-9}} = 0.524$$

This is close enough to use for the next guess

$$[H^+] = 4.15 \cdot 10^{-9} = e^{-2.303 \cdot pH}$$

$$pH = \frac{\ln (4.15 \cdot 10^{-9})}{-2.303} = 8.38$$

Using this pH and the current values of free H_2S, NH_3, begin again the successive substitution procedure for species concentrations and continue until a final solution is reached (achieving electrical neutrality). In most cases, several more pH trials may be required.

The final solution is

pH = 8.38

	Vapor Composition		Liquid Composition	
	lb/hr	mole/hr	wt. fr.	mole fr.
NH_3	48	2.82	.036	.0384
H_2S	49.7	1.46	.018	.0096
H_2O	114	6.33	.946	.9520

SECTION 6

COMPARISONS AND EVALUATIONS BETWEEN CALCULATED AND MEASURED DATA

Information in this section will be discussed in the following order:

a) Evaluation of Van Krevelen prediction model
b) Evaluation of SWEQ prediction model
c) Evaluation of new NH_3-H_2S-H_2O and NH_3-CO_2-H_2S-H_2O data
d) Ammonia fixation by carboxylic acids and release of NH_3 by addition of caustic

These subjects will be discussed by frequent referral to data summarized in Tables 18 to 27 which contain comparisons between calculated and measured vapor-liquid equilibrium data. Not all literature data were examined in this project because of the limited scope of the project. However, an attempt was made to examine as much data as possible. Table 28 summarizes various references collected during the project. This table also indicates the type found in each reference and whether the data were used for modeling purposes. Tables 29, 30, and 31 give summaries of deviation errors between calculated and measured partial pressures in Tables 18 to 27 for NH_3, CO_2, and H_2S respectively.

In developing the SWEQ model, some individual experimental points have been ignored and some entire data sets have been ignored. As a general policy, individual experimental points in a given set of measurements have been ignored in developing the correlation model when deviation errors from these points appeared to be radically difference from the main set of data. Entire sets of published data were ignored when deviations appeared to have little or no definite pattern and were also very large. When this has occurred, the data ignored and reasons for ignoring are noted at the bottom of the table.

Evaluation of Van Krevelen Model

The Van Krevelen prediction model which applies when NH_3/H_2S ratios are greater than 1.5 was derived by Van Krevelen et al[1] from low temperature data. These are compared with Tables 20 to 27 where columns headed VK represent predicted partial pressures from the Van Krevelen model[a] and columns headed MEAS represent measured partial pressure data. The following is a summary of the various comparisons.

---

[a] A listing of the Van Krevelen computer program is given in the Appendix.

Reproduced from best available copy.

TABLE 18. H_2S-H_2O, NH_3-H_2S-H_2O, AND NH_3-H_2O SYSTEMS, COMPARISON OF CALCULATED AND MEASURED DATA OF MILES AND WILSON[21] AND OF CLIFFORD AND HUNTER[17]

Temp. °C	Moles/Kg of Soln. NH_3	CO_2	H_2S	Partial Pressure, mm Hg NH_3 VK	NH_3 API	NH_3 MEAS	H_2S VK	H_2S API	H_2S MEAS	
80.	0.000	0.000	0.054					1068.6	951.3	
80.	0.000	0.000	0.297					5932.6	6185.8	
80.	0.000	0.000	0.509					10168.1	9978.1	
80.	0.000	0.000	0.515					10297.7	9978.1	
120.	0.000	0.000	0.047					1166.7	1194.3	
120.	0.000	0.000	0.240					4932.2	4797.8	
120.	0.000	0.000	0.341					8422.4	8427.1	Miles
150.	0.000	0.000	0.044					1177.5	1344.2	
150.	0.000	0.000	0.136					3637.5	4161.8	and
150.	0.000	0.000	0.232					6223.5	6917.5	
80.	0.994	0.000	1.358	0.0	5.1	4.3		8160.6	8556.3	Wilson
80.	0.914	0.000	0.925		12.0	12.1		2399.0	2388.5	
80.	4.339	0.000	4.157		85.4	72.4		8670.7	12144.3	
80.	2.159	0.000	1.066	137.1	127.7	136.5	349.0	380.8	319.0	Data
80.	6.469	0.000	5.553		208.7	208.9		7652.1	9512.8	
80.	4.828	0.000	4.258	296.9	399.6	465.3	1225.1	2244.7	1912.9	
80.	7.399	0.000	4.348	342.7	479.8	597.7	1056.7	1964.6	1918.1	
80.	4.535	0.000	1.015	384.0	442.5	574.4	99.2	99.1	94.6	
80.	13.705	0.000	2.831	776.5	2023.3	2373.0	172.4	173.1	156.1	
80.	14.358	0.000	3.528	775.3	2099.5	2285.1	233.1	269.6	241.4	
120.	0.515	0.000	0.696		24.9	23.8		6281.3	6410.3	
120.	1.072	0.000	0.946		106.3	95.1		4447.1	4627.1	
120.	0.959	0.000	0.477	170.1	174.2	182.5	1024.5	871.8	915.1	
120.	0.435	0.000	0.178	91.8	87.8	81.2	285.8	249.2	333.5	
120.	0.519	0.000	0.108	145.8	135.9	177.3	65.8	62.3	82.7	
120.	1.933	0.000	0.414	505.2	521.6	568.7	246.6	234.1	280.7	
120.	8.499	0.000	1.698	1605.3	2583.4	3179.5	762.4	738.8	972.8	
120.	0.011	0.000	0.001	3.6	3.1	2.1	0.1	0.1	0.6	
60.	3.452	0.000	0.000	181.5	214.7	241.4				
60.	8.055	0.000	0.000	324.9	634.0	627.1				
60.	13.155	0.000	0.000	395.6	1342.8	1442.4				
60.	19.342	0.000	0.000	407.3	2705.6	2957.2				
60.	23.000	0.000	0.000	387.6	4178.0	4559.9				Clifford
60.	27.066	0.000	0.000	365.2	5610.8	6079.9				
100.	3.452	0.000	0.000	660.9	711.4	770.3				and
100.	8.675	0.000	0.000	1229.3	2065.5	2311.0				
100.	12.358	0.000	0.000	1416.4	3255.6	3867.2				Hunter
100.	17.386	0.000	0.000	1491.6	5258.9	6979.5				
140.	0.555	0.000	0.000	302.8	294.4	299.9				Data
140.	3.285	0.000	0.000	1530.7	1788.9	1825.8				
140.	5.692	0.000	0.000	2389.1	3166.1	3376.0				
140.	7.829	0.000	0.000	2808.2	4435.9	4927.0				

TABLE 19. NH_3-H_2S-H_2O SYSTEM, COMPARISON OF CALCULATED AND MEASURED DATA OF TERRES[29]

Temp. °C	Moles/Kg of Soln.			Partial Pressure, mm Hg					
				NH_3			H_2S		
	NH_3	CO_2	H_2S	VK	API	MEAS	VK	API	MEAS
20.	0.810	0.000	0.411	4.3	4.2	0.0	4.9	5.6	53.3
20.	1.574	0.000	0.783	8.3	8.8	0.0	8.3	10.1	65.6
20.	3.975	0.000	1.998	19.3	26.1	0.0	16.8	24.6	130.1
20.	4.727	0.000	2.356	22.7	33.0	5.6	18.1	28.0	154.8
20.	5.526	0.000	2.758	25.9	40.7	13.0	19.6	32.3	190.0
40.	1.356	0.000	0.684	18.2	17.8	8.2	30.1	29.1	92.0
40.	3.453	0.000	1.719	44.0	52.4	22.2	59.7	67.8	183.4
40.	4.234	0.000	2.130	52.3	66.7	26.9	69.4	84.2	220.6
40.	5.484	0.000	2.746	65.6	93.9	38.4	78.1	100.2	293.2
60.	1.891	0.000	0.954	57.0	55.1	25.5	123.2	130.4	134.1
60.	3.253	0.000	1.631	94.0	102.8	48.5	181.3	213.2	205.0
60.	3.993	0.000	1.998	114.1	131.7	76.1	205.1	255.4	250.9
60.	5.285	0.000	2.656	145.0	186.7	145.0	240.2	331.2	365.0

Reproduced from best available copy.

TABLE 20. NH_3-H_2S-H_2O SYSTEM, COMPARISON OF CALCULATED AND MEASURED DATA OF VAN KREVELEN, ET AL.

Temp. °C	Moles/Kg of Soln. NH_3	CO_2	H_2S	Partial Pressure, mm Hg NH_3 VK	NH_3 API	NH_3 MEAS	H_2S VK	H_2S API	H_2S MEAS
20.	0.300	0.000	0.185	1.3	1.2	0.0	3.6	4.0	4.2
20.	0.595	0.000	0.375	2.4	2.3	0.0	7.4	8.5	8.2
20.	1.190	0.000	1.165	6.6	7.1	0.0	21.5	28.1	18.4
20.	2.350	0.000	1.540	8.5	9.5	0.0	26.8	37.6	27.1
20.	2.920	0.000	1.890	10.6	12.5	0.0	29.6	44.1	34.5
20.	0.295	0.000	0.140	1.7	1.6	0.0	1.5	1.7	0.0
20.	0.585	0.000	0.285	3.2	3.1	0.0	3.2	3.6	3.0
20.	1.190	0.000	0.580	6.5	6.6	0.0	6.1	7.2	6.7
20.	1.780	0.000	0.860	9.6	10.4	0.0	8.5	10.4	9.4
20.	2.400	0.000	1.150	12.7	14.8	0.0	10.5	13.4	12.2
20.	2.930	0.000	1.440	15.8	18.3	0.0	13.8	17.4	15.8
20.	0.288	0.000	0.110	1.8	1.7	0.0	0.9	1.0	0.8
20.	0.580	0.000	0.220	3.9	3.7	0.0	1.6	1.8	1.7
20.	1.175	0.000	0.455	7.6	7.8	0.0	3.3	3.7	3.6
20.	1.780	0.000	0.690	11.2	12.3	0.0	4.8	5.6	4.9
20.	2.260	0.000	0.875	14.0	16.2	0.0	5.8	7.0	6.0
20.	2.860	0.000	1.110	17.3	21.4	0.0	7.0	8.7	6.7
20.	0.288	0.000	0.070	2.3	2.1	0.0	0.3	0.3	0.3
20.	0.575	0.000	0.145	4.6	4.5	0.0	0.6	0.6	0.4
20.	1.150	0.000	0.290	9.0	9.3	0.0	1.2	1.3	1.1
20.	1.730	0.000	0.435	13.2	14.7	0.0	1.7	1.9	1.6
20.	2.310	0.000	0.585	17.1	20.6	0.0	2.2	2.5	2.3
20.	2.920	0.000	0.730	21.2	27.2	0.0	2.6	3.0	2.8
20.	0.288	0.000	0.060	2.4	2.2	0.0	0.2	0.2	0.0
20.	0.585	0.000	0.120	5.0	4.8	0.0	0.4	0.4	0.3
20.	1.060	0.000	0.220	8.6	9.1	0.0	0.7	0.7	0.9
20.	1.720	0.000	0.355	13.8	15.5	0.0	1.1	1.2	1.1
20.	2.270	0.000	0.440	18.0	21.7	0.0	1.2	1.3	1.4
20.	2.870	0.000	0.558	22.2	28.8	0.0	1.5	1.4	1.6
20.	3.460	0.000	0.590	26.7	37.3	0.0	1.3	1.4	1.3
40.	0.300	0.000	0.185	3.2	2.9	0.0	14.3	12.7	13.3
40.	0.595	0.000	0.375	6.1	5.6	0.0	29.5	27.1	26.9
40.	1.190	0.000	1.165	16.9	17.2	0.0	85.2	89.8	0.0
40.	2.350	0.000	1.540	21.7	23.0	0.0	106.3	119.9	0.0
40.	2.920	0.000	1.890	27.2	30.3	0.0	117.2	148.7	125.4
40.	0.295	0.000	0.140	4.3	3.8	0.0	6.1	5.5	0.0
40.	0.585	0.000	0.285	8.3	7.6	0.0	12.7	11.6	12.7
40.	1.190	0.000	0.580	16.5	16.8	0.0	24.4	23.2	23.6
40.	1.780	0.000	0.860	24.5	25.8	0.0	35.6	33.3	32.6
40.	2.400	0.000	1.150	32.6	35.3	0.0	41.6	43.2	43.2
40.	2.930	0.000	1.440	38.4	43.6	0.0	51.6	56.1	54.4
40.	0.288	0.000	0.110	4.7	4.2	0.0	3.5	3.1	3.7
40.	0.580	0.000	0.220	9.9	9.1	0.0	6.4	5.8	6.9
40.	1.175	0.000	0.455	19.4	18.8	0.0	13.8	12.1	12.5
40.	1.780	0.000	0.693	28.7	29.6	0.0	18.9	18.8	18.8
40.	2.260	0.000	0.875	35.9	38.8	0.0	23.8	22.5	22.3
40.	2.860	0.000	1.110	44.4	58.9	0.0	27.9	28.1	31.6
40.	0.288	0.000	0.070	5.8	5.2	0.0	1.1	1.0	1.3
40.	0.575	0.000	0.145	11.8	10.8	0.0	2.4	2.1	0.0
40.	1.150	0.000	0.290	23.8	22.4	0.0	4.6	4.1	4.6
40.	1.730	0.000	0.435	33.7	35.1	0.0	6.7	6.0	6.6
40.	2.310	0.000	0.585	43.8	48.5	0.0	8.8	8.0	8.1
40.	2.920	0.000	0.730	54.2	64.0	0.0	10.4	9.5	10.8
40.	0.288	0.000	0.060	6.1	5.4	0.0	0.8	0.7	0.0
40.	0.585	0.000	0.120	12.7	11.7	0.0	1.5	1.3	1.5
40.	1.060	0.000	0.220	22.5	21.8	0.0	2.7	2.4	2.6
40.	1.720	0.000	0.355	35.4	36.9	0.0	4.3	3.8	4.0
40.	2.270	0.000	0.440	46.2	51.3	0.0	4.8	4.2	5.0
40.	2.870	0.000	0.558	56.9	67.6	0.0	5.8	5.1	5.9
40.	3.460	0.000	0.590	68.2	86.9	0.0	5.4	4.6	4.7
60.	0.300	0.000	0.185	7.3	6.3	0.0	44.2	40.6	39.6
60.	0.595	0.000	0.375	13.9	12.2	0.0	91.3	86.7	0.0
60.	1.190	0.000	1.165	38.7	37.4	0.0	263.9	284.6	182.3
60.	2.350	0.000	1.540	49.6	50.1	0.0	329.5	381.7	0.0
60.	2.920	0.000	1.890	62.3	65.7	0.0	363.3	448.6	310.5
60.	0.295	0.000	0.140	9.9	8.3	0.0	19.8	17.8	15.6
60.	0.585	0.000	0.285	18.9	16.4	0.0	39.4	37.7	35.5
60.	1.190	0.000	0.580	37.8	34.4	0.0	75.6	75.6	66.9
60.	1.780	0.000	0.860	56.8	53.6	0.0	104.8	108.5	98.6
60.	2.400	0.000	1.150	74.6	75.4	0.0	129.0	148.5	135.9
60.	2.930	0.000	1.440	87.7	92.7	0.0	159.9	182.3	151.9
60.	0.288	0.000	0.110	10.8	9.1	0.0	18.7	18.1	11.8
60.	0.580	0.000	0.220	22.6	19.5	0.0	19.8	18.9	20.5
60.	1.175	0.000	0.455	44.3	40.4	0.0	40.4	39.6	38.6
60.	1.780	0.000	0.690	65.7	63.2	0.0	58.5	59.0	54.7
60.	2.260	0.000	0.875	82.8	82.4	0.0	71.3	73.6	68.8
60.	2.864	0.000	1.110	101.5	107.6	0.0	86.5	92.8	94.2
60.	0.288	0.000	0.070	13.3	11.2	0.0	3.5	3.3	0.8
60.	0.575	0.000	0.145	26.9	23.3	0.0	7.3	6.9	8.7
60.	1.150	0.000	0.290	52.5	48.0	0.0	14.2	13.5	14.5
60.	1.730	0.000	0.435	77.1	74.5	0.0	20.6	19.7	19.4
60.	2.310	0.000	0.585	100.2	102.3	0.0	27.2	26.2	26.0
60.	2.920	0.000	0.730	123.4	134.2	0.0	32.3	31.4	31.6
60.	0.288	0.000	0.060	13.9	11.7	0.0	2.5	2.3	2.6
60.	0.585	0.000	0.120	29.0	25.1	0.0	4.7	4.4	4.9
60.	1.060	0.000	0.220	51.3	46.6	0.0	8.5	8.0	9.4
60.	1.720	0.000	0.355	80.9	78.4	0.0	13.2	12.4	12.9
60.	2.270	0.000	0.440	105.7	108.1	0.0	16.9	15.9	16.8
60.	2.870	0.000	0.558	130.2	141.5	0.0	18.8	16.8	18.3
60.	3.460	0.000	0.590	156.1	148.4	0.0	16.6	15.2	17.6

TABLE 21. H_2S IN AQUEOUS BUFFER SOLUTIONS, COMPARISON OF CALCULATED AND MEASURED DATA OF SHIH, ET AL.[26]

pH	Temp. °C	Moles/Kg of Soln. NH_3	Moles/Kg of Soln. CO_2	Moles/Kg of Soln. H_2S	Partial Pressure, mm Hg H_2S VK	H_2S API	H_2S MEAS
7.00	80.	0.000	0.000	0.010		59.3	64.0
7.00	100.	0.000	0.000	0.010		60.1	96.0
7.00	120.	0.000	0.000	0.010		61.8	104.0
7.00	140.	0.000	0.000	0.010		68.8	117.0
7.00	160.	0.000	0.000	0.010		86.4	125.0
7.00	185.	0.000	0.000	0.010		136.7	133.0
7.00	80.	0.000	0.000	0.010		10.1	16.1
7.90	100.	0.000	0.000	0.010		11.5	19.6
7.83	120.	0.000	0.000	0.010		12.4	22.7
7.80	140.	0.000	0.000	0.010		15.0	25.4
7.77	160.	0.000	0.000	0.010		20.7	29.5
7.75	185.	0.000	0.000	0.010	0.0	42.2	32.3
7.70							

TABLE 22. NH_3-CO_2-H_2O AND CO_2-H_2O SYSTEMS, COMPARISON OF CALCULATED AND MEASURED DATA OF VAN KREVELEN, ET AL.[1] AND DATA FROM LANGE'S HANDBOOK[20]

Temp. °C	Moles/Kg of Soln.			Partial Pressure, mm Hg						
				NH_3			CO_2			
	NH_3	CO_2	H_2S	VK	API	MEAS	VK	API	MEAS	
20.	0.490	0.123	0.000	3.2	3.1	0.0	0.3	0.2	0.2	
20.	1.960	0.660	0.000	8.2	9.0	9.4	0.9	0.8	0.8	
20.	1.990	0.490	0.000	11.4	12.8	13.0	0.3	0.3	0.3	
20.	2.010	0.545	0.000	10.7	12.8	12.5	0.4	0.3	0.4	
40.	0.490	0.316	0.000	3.1	2.8	0.0	20.6	23.3	27.0	
40.	0.500	0.257	0.000	4.7	4.3	4.4	11.0	9.0	10.1	
40.	0.980	0.609	0.000	5.2	5.1	5.1	41.1	33.6	0.0	
40.	0.980	0.623	0.000	5.0	4.0	0.0	45.9	37.5	46.5	
40.	1.000	0.513	0.000	7.9	7.6	9.0	18.1	14.5	16.7	
40.	2.000	1.026	0.000	12.5	13.1	11.5	25.9	21.4	23.5	Van Krevelen
40.	2.000	0.540	0.000	28.4	30.0	0.0	2.5	2.1	2.4	
60.	0.500	0.098	0.000	22.9	19.7	21.5	3.4	3.4	3.7	Data
60.	0.500	0.319	0.000	8.1	7.2	7.0	101.1	95.2	93.0	
60.	1.000	0.195	0.000	43.2	39.1	42.0	4.6	4.4	4.1	
60.	1.000	0.364	0.000	30.0	27.1	29.2	23.1	22.4	20.4	
60.	1.000	0.678	0.000	11.6	10.8	12.0	220.1	203.0	215.0	
60.	2.000	0.370	0.000	81.6	81.1	95.0	4.6	4.6	5.3	
60.	2.000	0.696	0.000	54.8	54.0	61.0	25.6	23.2	29.0	
60.	2.000	0.998	0.000	34.1	33.7	36.0	94.3	90.8	86.0	
60.	2.000	1.338	0.000	17.1	17.6	18.0	379.2	355.9	394.0	
0.	0.000	0.076	0.000	0.0	0.0	0.0	0.0	895.4	760.0	
20.	0.000	0.039	0.000	0.0	0.0	0.0	0.0	791.0	760.0	
40.	0.000	0.024	0.000	0.0	0.0	0.0	0.0	718.6	760.0	Lange's Handbook
60.	0.000	0.016	0.000	0.0	0.0	0.0	0.0	668.6	760.0	

TABLE 23. NH_3-CO_2-H_2O SYSTEM, COMPARISON OF CALCULATED AND MEASURED DATA OF OTSAKE, ET AL.[22]

Temp. °C	Moles/Kg of Soln.			Partial Pressure, mm Hg					
				NH_3			CO_2		
	NH_3	CO_2	H_2S	VK	API	MEAS	VK	API	MEAS
20.	0.998	0.820	0.000	0.6	0.6	0.5	56.7	45.6	55.0
20.	2.331	0.298	0.000	17.6	21.1	20.3	0.1	0.0	0.5
20.	1.720	1.431	0.000	0.0	0.7	0.7	0.0	84.3	105.2
20.	4.157	0.500	0.000	29.1	43.7	48.6	0.0	0.0	0.1
20.	2.877	1.903	0.000	2.0	2.4	3.1	34.7	28.4	53.5
20.	5.598	2.836	0.000	7.7	11.1	11.2	6.1	5.0	7.3
20.	7.487	3.915	0.000	0.0	13.1	15.1	7.9	6.7	13.9
40.	0.732	0.763	0.000	133.9	308.4	285.3	0.1	0.1	0.3
40.	10.734	2.579	0.000	116.0	277.3	322.0	1.0	0.9	1.1
40.	2.719	1.334	0.000	16.7	18.4	19.4	23.5	20.0	22.9
60.	1.014	1.268	0.000	14.2	14.5	22.0	447.5	410.2	442.0
60.	2.866	0.938	0.000	77.5	82.1	177.2	22.2	22.0	3.4
60.	5.790	2.280	0.000	111.7	147.0	353.3	37.2	36.7	4.1
60.	6.860	2.984	0.000	137.6	187.9	364.2	21.6	21.4	14.9
60.	6.794	3.613	0.000	60.0	87.1	101.3	207.0	198.9	271.7
60.	7.853	3.495	0.000	104.6	159.0	313.0	74.0	72.3	31.0
60.	8.291	2.838	0.000	166.9	269.9	485.0	22.2	22.1	20.0
80.	2.824	1.218	0.000	123.5	122.0	108.4	223.9	267.2	256.2
80.	3.846	0.816	0.000	262.9	305.1	297.3	27.3	33.0	41.6
80.	4.891	0.405	0.000	434.9	527.0	490.0	3.3	4.2	10.6
80.	4.486	1.563	0.000	224.7	252.2	214.5	115.0	130.2	100.5
80.	7.352	0.564	0.000	585.2	685.2	802.0	2.7	3.3	19.0
100.	2.601	1.302	0.000	176.3	185.7	157.7	1203.0	1757.0	1211.0
100.	4.891	0.407	0.000	765.0	924.1	923.0	12.6	19.9	43.0
100.	4.474	1.563	0.000	407.5	473.4	427.0	409.6	625.1	645.0
100.	6.271	0.936	0.000	823.0	1099.6	1022.0	42.5	67.3	107.0

TABLE 24. NH_3-CO_2-H_2S-H_2O SYSTEM, COMPARISON OF CALCULATED AND MEASURED DATA OF CARDON AND WILSON[5]

Temp. °C	Moles/Kg of Soln.			Partial Pressure, mm Hg								
				NH_3			CO_2			H_2S		
	NH_3	CO_2	H_2S	VK	API	MEAS	VK	API	MEAS	VK	API	MEAS
50.	5.445	1.706	2.689	15.5	22.3	30.5	195.1	309.8	239.9	594.6	1286.2	1132.2
50.	10.142	2.665	3.711	67.8	122.3	263.2	25.2	62.6	54.3	114.6	442.3	540.8
50.	1.511	0.055	0.172	49.8	49.2	49.2a)	0.3	0.3	2.3a)	2.6	2.4	0.8a)
80.	5.606	1.485	3.008	72.4	108.5	164.4	975.4	1871.1	1613.0	1378.6	4748.7	3968.2
80.	1.963	0.027	0.165	211.7	195.9	164.4a)	0.6	0.8	7.6a)	7.2	6.8	28.4a)
80.	4.543	2.189	1.774	30.7	52.2	95.1	4152.7	4706.4	3453.6	1215.4	4267.5	2585.8
80.	4.181	1.999	1.487	29.5	47.4	127.7	4024.3	4362.3	3458.7	1117.1	3519.8	2517.8
80.	1.048	0.284	0.083	86.6	73.8	102.4	26.0	31.9	65.5	12.1	13.2	18.4
80.	0.542	0.460	0.093	0.8	4.3	0.8	0.0	2656.3	2436.6	0.0	351.2	246.1
80.	0.752	0.137	0.499	13.5	15.3	7.8	312.5	275.7	346.9	1040.2	767.1	589.4
80.	0.582	0.384	0.049	14.3	13.1	29.5	640.2	647.7	453.4	57.8	60.3	47.6
80.	2.692	0.995	1.117	42.2	49.5	102.4	1098.7	1319.0	987.5	968.9	1720.9	1354.5
80.	15.101	2.748	3.769	579.9	1425.6	2176.6	35.1	121.0	149.9	60.1	626.6	847.9
110.	2.124	0.754	1.155	41.6	112.3	285.9	11867.4	7471.6	5976.5	7736.3	5470.7	4616.8
110.	0.552	0.541	0.115	0.8	17.7	15.5	0.0	10589.9	9145.7	0.0	843.8	801.3
110.	0.597	0.072	0.166	98.4	98.5	180.3	183.4	176.2	169.1	160.8	155.5	172.2
110.	5.676	2.511	1.281	249.6	489.7	353.1	5724.5	10211.2	10848.1	320.2	3741.9	4425.5
110.	2.645	1.566	0.786	42.2	118.8	563.5a)	26855.9	15998.6	9988.4	2594.0	4186.2	7207.0
120.	2.152	0.894	0.166	600.6	630.1	734.1	25.1	54.6	103.4	48.2	49.2	67.2
120.	0.259	0.231	0.138	0.0	12.0	19.1	0.0	7296.7	6860.6	0.0	1269.3	1623.4
120.	0.853	0.426	0.306	34.7	76.6	93.6	9596.0	6208.4	5619.8	3036.6	1502.6	1483.8
120.	0.185	0.011	0.022	25.9	23.8	16.3a)	26.6	58.2	58.3	21.3	22.0	22.4
120.	0.883	0.028	0.083	0.0	4.2	46.6	0.0	899.5	752.8	0.0	787.3	563.0

a) These points ignored in computing averages because they represent extreme deviations which are probably due to major error in the measured values. In the third and fifth runs, the entire run was suspected, so the entire run was ignored.

Reproduced from best available copy.

TABLE 25. NH_3-CO_2-H_2S-H_2O SYSTEM, COMPARISON OF CALCULATED AND MEASURED DATA OF BADGER AND SILVER[15]

Temp. °C	Moles/Kg of Soln.			Partial Pressure, mm Hg								
				NH_3			CO_2			H_2S		
	NH_3	CO_2	H_2S	VK	API	MEAS	VK	API	MEAS	VK	API	MEAS
20.	1.189	0.410	0.189	3.9	4.0	4.1	1.9	1.7	1.5	3.6	3.6	3.2
20.	1.194	0.490	0.194	2.9	3.0	2.9	3.7	3.2	3.5	5.4	5.4	5.1
20.	1.390	0.495	0.390	2.9	3.0	2.4	4.2	3.9	3.7	13.7	14.1	12.6
20.	1.045	0.500	0.045	2.8	2.8	2.7	3.6	3.8	3.7	1.1	1.1	0.0
20.	1.380	0.638	0.380	1.6	1.7	1.5	13.2	12.1	13.1	26.9	26.7	27.0
20.	1.097	0.660	0.097	1.4	1.5	1.3	14.1	11.9	12.1	6.1	5.7	5.3
20.	1.192	0.670	0.192	1.4	1.4	1.3	16.0	13.8	13.1	13.9	13.3	11.1
20.	1.196	0.688	0.196	1.3	1.3	1.3	18.6	15.8	19.0	15.8	15.0	15.3
20.	1.192	0.700	0.192	1.2	1.2	0.9	20.6	17.9	20.5	16.6	15.7	15.9
20.	1.193	0.745	0.193	0.9	1.0	0.9	30.2	25.7	29.2	22.1	20.5	27.4
20.	1.092	0.770	0.092	0.8	0.8	0.7	36.2	31.3	35.2	11.4	10.3	12.2
20.	1.088	0.790	0.088	0.7	0.7	0.0	43.4	36.1	42.4	12.5	11.3	0.0
20.	1.095	0.800	0.095	0.7	0.7	0.0	47.8	40.3	45.1	14.7	13.1	0.0
20.	1.088	0.815	0.088	0.6	0.6	0.5	55.1	45.1	0.0	15.2	13.4	13.1
20.	1.095	0.818	0.095	0.6	0.6	0.6	56.9	46.4	0.0	16.9	14.9	16.9

TABLE 26. NH_3-H_2O SYSTEM, COMPARISON OF CALCULATED AND MEASURED DATA OF BREITENBACH AND PERMAN[16,23]

Temp. °C	Moles/Kg of Soln.			Partial Pressure, mm Hg		
				NH_3		
	NH_3	CO_2	H_2S	VK	API	MEAS
20.	1.174	0.000	0.000	12.8	12.7	12.0
20.	1.466	0.000	0.000	14.8	16.3	15.0
20.	1.762	0.000	0.000	17.4	20.1	18.2
20.	2.349	0.000	0.000	22.5	28.1	24.9
20.	2.936	0.000	0.000	27.2	36.8	31.7
20.	4.404	0.000	0.000	37.4	62.2	50.0
20.	5.872	0.000	0.000	45.9	93.4	69.6
20.	8.808	0.000	0.000	58.1	177.7	114.0
20.	11.744	0.000	0.000	65.4	300.4	166.0
20.	14.680	0.000	0.000	69.1	474.1	227.0
20.	17.616	0.000	0.000	70.0	724.4	298.0
20.	23.488	0.000	0.000	66.5	1551.9	470.0
20.	29.360	0.000	0.000	59.3	3117.9	686.0
20.	35.232	0.000	0.000	50.7	6011.1	945.0
20.	41.104	0.000	0.000	42.2	11274.0	1170.0
20.	46.976	0.000	0.000	34.4	20703.7	1450.0
40.	1.762	0.000	0.000	44.6	47.6	45.0
40.	2.936	0.000	0.000	69.5	85.7	76.5
40.	5.872	0.000	0.000	117.4	207.6	167.0
40.	11.744	0.000	0.000	167.5	608.1	395.0
40.	17.616	0.000	0.000	179.1	1335.4	692.0
40.	29.360	0.000	0.000	151.8	4769.3	1520.0
40.	41.104	0.000	0.000	104.0	14308.1	2760.0
60.	0.587	0.000	0.000	36.4	31.4	30.2
60.	0.940	0.000	0.000	57.1	51.2	48.7
60.	1.468	0.000	0.000	86.5	82.4	77.0
60.	2.936	0.000	0.000	159.8	177.8	165.0
60.	4.404	0.000	0.000	219.2	287.6	261.0
60.	5.872	0.000	0.000	268.6	413.5	361.0
60.	8.808	0.000	0.000	340.2	720.5	583.0
60.	11.744	0.000	0.000	383.0	1115.7	834.0

Reproduced from best available copy.

TABLE 27. NH_3-CO_2-H_2S-H_2O SYSTEM, COMPARISON OF CALCULATED AND MEASURED DATA OF VAN KREVELEN, ET AL[1]

Temp. °C	Moles/Kg of Soln.			Partial Pressure, mm Hg								
				NH_3			CO_2			H_2S		
	NH_3	CO_2	H_2S	VK	API	MEAS	VK	API	MEAS	VK	API	MEAS
20.	1.140	0.410	0.180	3.5	3.6	0.0	2.1	1.9	0.0	3.7	3.7	4.2
20.	1.240	0.750	0.291	0.7	0.8	0.0	44.7	38.0	0.0	46.2	44.0	49.0
20.	2.160	0.950	0.360	3.7	4.0	0.0	6.4	5.9	0.0	13.4	12.7	14.0
20.	2.150	0.400	0.600	8.9	9.9	0.0	0.5	0.5	0.0	7.3	7.9	8.4
20.	2.250	1.400	0.210	1.7	1.9	0.0	30.7	26.5	0.0	19.7	16.5	18.0
20.	0.790	0.250	0.180	2.6	2.6	0.0	1.7	1.5	0.0	3.7	3.9	4.5
40.	1.170	0.410	0.184	10.6	10.3	0.0	10.2	8.9	0.0	11.3	10.7	11.7
40.	1.140	0.410	0.180	10.0	9.7	0.0	11.0	9.6	0.0	11.6	10.9	12.3
40.	1.130	0.210	0.290	14.1	13.6	0.0	3.1	2.8	0.0	12.0	11.2	12.1
40.	2.160	0.940	0.360	11.3	11.9	0.0	30.4	27.6	0.0	33.7	35.2	38.4
40.	2.150	0.400	0.600	23.6	24.8	0.0	3.5	3.5	0.0	24.0	24.9	27.0
40.	0.700	0.104	0.350	5.9	5.5	0.0	5.1	4.5	0.0	33.1	30.7	32.3
40.	0.790	0.250	0.180	7.3	6.9	0.0	8.6	7.7	0.0	12.5	11.6	13.3
40.	0.740	0.380	0.160	3.3	3.2	0.0	42.0	35.9	0.0	29.3	26.0	27.0
40.	2.250	1.400	0.210	5.7	6.2	0.0	128.0	109.4	0.0	40.5	43.4	37.6
60.	1.170	0.410	0.184	26.1	24.0	0.0	43.2	43.9	0.0	29.3	32.6	29.5
60.	1.140	0.410	0.180	24.0	22.7	0.0	46.3	46.8	0.0	30.0	33.3	30.0
60.	1.130	0.210	0.290	33.3	30.3	0.0	14.0	14.6	0.0	34.1	35.5	32.0
60.	2.160	0.950	0.360	28.7	29.0	0.0	131.1	137.0	0.0	74.7	107.0	84.4
60.	2.150	0.400	0.600	55.0	55.3	0.0	17.3	19.7	0.0	67.2	79.6	77.5
60.	2.250	1.340	0.200	18.6	19.5	0.0	360.4	352.0	0.0	59.3	95.0	59.5
60.	0.700	0.104	0.350	13.9	12.4	0.0	21.6	22.2	0.0	96.6	94.9	80.4
60.	0.790	0.250	0.180	17.9	15.9	0.0	36.2	36.4	0.0	34.1	35.3	32.0
60.	0.740	0.360	0.150	10.1	9.2	0.0	119.3	114.4	0.0	55.0	58.3	53.5
60.	1.020	0.620	0.140	9.3	8.9	0.0	285.5	265.9	0.0	70.0	79.2	63.7
60.	1.294	0.656	0.124	19.4	18.3	0.0	121.3	118.4	0.0	29.7	35.9	25.0
60.	1.289	0.645	0.234	15.1	14.4	0.0	177.2	174.3	0.0	80.3	96.4	77.0

TABLE 28. SUMMARY OF REFERENCES TO EXPERIMENTAL DATA

Reference	Type of Data	Used in Correlation
5	NH_3-CO_2-H_2S-H_2O 50°C to 120°C	yes
15	NH_3-CO_2-H_2S-H_2O 20°C	yes
16	NH_3-H_2O 0°C to 60°C	yes
17	NH_3-H_2O 97°C to 147°C	yes
18	NH_3-CO_2-H_2S-H_2O 20°C	no
19	NH_3-CO_2-H_2O 20°C to 40°C	no
20	CO_2-H_2O 0°C to 60°C	yes
21	H_2S-H_2O 80°C to 150°C	yes
	NH_3-H_2S-H_2O 80°C to 120°C	yes
22	NH_3-CO_2-H_2O 20°C to 100°C	yes
23	NH_3-H_2O 0°C to 60°C	yes
24	NH_3-H_2O 0°C to 60°C	yes
25	NH_3-CO_2-H_2O 20°C to 40°C	no
26	H_2S-H_2O (Buffered) 80°C to 185°C	yes

(continued)

TABLE 28. (continued)

27	NH_3-CO_2-H_2O 70°C to 120°C	no
28	NH_3-CO_2-H_2O Phase diagrams 60°C to 170°C	no
29	NH_3-H_2S-H_2O 20°C to 60°C	yes
1	NH_3-CO_2-H_2O NH_3-H_2S-H_2O NH_3-CO_2-H_2S-H_2O 20°C to 60°C	yes yes yes
30	NH_3-H_2O 114°C to 317°C	no
31	CO_2-H_2O 270°C to 550°C	no
32	H_2S-H_2O 160°C to 330°C	no
33	NH_3-H_2S-H_2O 70°C to 90°C	no
34	H_2S-H_2O 25°C	no
35	H_2S-H_2O-Salt 150°C to 330°C	no
36	H_2S-H_2O H_2S-CH_4-H_2O 71°C to 140°C	no
37	NH_3-CO_2-H_2O 60°C to 150°C	no

More references are given in I. Wichterle, J. Linek, and E. Hala, Vapor-Liquid Equilibrium Data Bibliography, Elsevier (1973). The references listed above are ones for which copies of the data have been obtained.

TABLE 29. SUMMARY OF DEVIATION ERRORS BETWEEN CALCULATED AND MEASURED AMMONIA PARTIAL PRESSURES

Partial Pressures in Table no.	Temp °C	Van Krevelen vs Meas. Data		API SWEQ vs Meas. Data	
		No. pts	Ave. Error %	No. pts	Ave. Error %
18	80	6	60	10	14
	120	6	29	8	17
	60	6	387	6	8
	100	4	130	4	18
	140	4	33	4	5
19 a)	20	5	184 a)	5	329 a)
	40	4	107 a)	4	150 a)
	60	4	60 a)	4	79 a)
22	20	4	15	4	3
	40	7	8	7	8
	60	9	8	9	8
23	20	7	45	7	11
	40	3	90	3	10
	60	7	139	7	81
	80	5	14	5	10
	100	4	15	4	9
24	50	3	98	3	43
	80	10	126	10	77
	110	5	115	5	35
	120	5	73	5	30
25	20	13	8	13	12
26 b)	20	16	242 b)	16	128 b)
	40	7	223 b)	7	84 b)
overall average ignoring data in Tables 23 & 30			72		24

a) These data appear to be of rather low quality and should be given very little weight.

b) These data are in disagreement with data for NH_3-H_2O in Table 22 by Clifford and Hunter. From our evaluation we believe the data of Clifford and Hunter to be more nearly correct, and more weight has been given to their data.

TABLE 30. SUMMARY OF DEVIATION ERRORS BETWEEN CALCULATED AND MEASURED CARBON DIOXIDE PARTIAL PRESSURES

Partial Pressure in Table no.	Temp. °C	Van Krevelen vs. Meas. Data		API SWEQ vs. Meas. Data	
		No. pts.	Ave. Error%	No. pts.	Ave. Error%
22	20	4	13	4	5
	40	8	8	8	13
	60	9	9	9	10
	0	--	--	1	18
	20	--	--	1	4
	40	--	--	1	6
	60	--	--	1	15
23 [a]	20	5	102 [a]	7	117 [a]
	40	3	40 [a]	3	66 [a]
	60	7	126 [a]	7	128 [a]
	80	5	128 [a]	5	91 [a]
	100	4	92	4	51 [a]
24	50	3	63	3	23
	80	9	63	10	29
	110	4	98	5	20
	120	3	148	5	25
25	20	15	8	15	12
	overall average ignoring data in Table 27		35		17

a) These data appear to be of rather low quality and should be given very little weight because deviations are large and have little apparent pattern.

TABLE 31. SUMMARY OF DEVIATION ERRORS BETWEEN CALCULATED AND MEASURED HYDROGEN SULFIDE PARTIAL PRESSURES

Partial Pressures in Table no.	Temp. °C	Van Krevelen vs. Meas. Data		API SWEQ vs. Meas. Data	
		No. pts.	Ave. Error%	No. pts.	Ave. Error%
18	80	--	--	4	5
	120	--	--	3	2
	150	--	--	3	13
	80	6	22	10	13
	120	6	44	8	44
19 [a]	20	5	787[a]	5	539[a]
	40	4	225[a]	4	182[a]
	60	4	23[a]	4	5[a]
20	20	30	10	30	14
	40	30	6	30	8
	60	30	9	30	12
21	80	--	--	2	50
	100	--	--	2	67
	120	--	--	2	75
	140	--	--	2	70
	160	--	--	2	44
	185	--	--	2	16
24	50	3	211	3	13
	80	9	139	10	47
	110	4	188	5	23
	120	3	46	5	18
25	20	15	10	15	11
27	20	6	12	6	12
	40	9	6	9	10
	60	12	8	12	20
overall average ignoring data in Table 23.			24		18

a) These data appear to be of rather low quality. Large and unreasonable adjustments would have to be made in the correlation model to correlate these data; therefore they were ignored.

Table No.	System	Temp. Range, °C	Ave. Error, % NH_3	CO_2	H_2S
20	NH_3-H_2S-H_2O	20°C to 60°C	---	---	8
22	NH_3-CO_2-H_2O	20°C to 60°C	9	9	---
25	NH_3-CO_2-H_2S-H_2O	20°C	8	8	10
27	NH_3-CO_2-H_2S-H_2O	20°C to 60°C	---	---	8

From this comparison, average errors are about 10% or less in these tables; however only data from 20° to 60°C are compared. When higher temperature data and other literature data are compared the agreement is not as good because of extrapolation errors. These comparisons are given in Tables 18, 19 24, and 25 where deviation errors can be summarized as follows.

Table No.	System	Temp. Range, °C	Ave. Error, % NH_3	CO_2	H_2S
18	NH_3-H_2S-H_2O	80°C to 120°C	139	---	58
19	NH_3-H_2S-H_2O	20°C to 60°C	122[b]	---	379[b]
23	NH_3-CO_2-H_2O	20°C to 100°C	65[b]	105[b]	---
24	NH_3-CO_2-H_2S-H_2O	50°C to 120°C	108	84	146

This comparison shows that deviation errors are baout 3 to 15 times higher than for the systems from which the correlation was derived. This conclusion doesn't change significantly even when suspected data noted at the bottom of this summary are ignored. Thus, it is concluded that the Van Krevelen model does well at temperatures from 20°C to 60°C which is the region from which it was derived, but its accuracy is much poorer at temperatures from 60° to 120°C which is the range of commercial interest for sour water strippers. Beychok[38] has recently proposed an NH_3 Henry's constant published by Edwards et al[4] which improves predicted NH_3 volatilities. By this method, the average error for NH_3 at 80°C in Table 29 is reduced from 60% to 23%.

Evaluation of SWEQ Model

The SWEQ model has the advantage that both low-temperature and high-temperature data were used in developing the model, thus it would be expected to give better results than the Van Krevelen model. A comparison of the API SWEQ model with the Van Krevelen model and with experimental data is given in Tables 18 to 27 under the heading API. At some of the conditions in these tables, direct comparison with the Van Krevelen model is not possible because the Van Krevelen modes does not permit the calculation of equilibrium data at NH_3/H_2S ratios less than 1.5 or for NH_3/total acid gas ratios less than unity. This condition occurred in the following cases.

[b] Measured data in Tables 19 and 23 are believed by the author to be unreliable. Data in Table 19 deviate radically. Large and unreasonable adjustments would have to be made in the model to correlate these data. Data in Table 23 exhibit large deviations with little apparent pattern.

Table No.	System	Temp. Range, °C
18	H_2S-H_2O	80°C to 150°C
	H_2S-NH_3-H_2O	80°C and 120°C
21	H_2S-buffer-H_2O	80°C to 185°C
22	CO_2-H_2O	0°C to 60°C
24	NH_3-CO_2-H_2S-H_2O (4 points)	80°C to 120°C

A comparison of the SWEQ model with the Van Krevelen model at low temperatures where the Van Krevelen model was derived gives the following results.

Table No.	System	Temp. Range °C	Ave. Error % NH_3		CO_2		H_2S	
			VK	SWEQ	VK	SWEQ	VK	SWEQ
20	NH_3-H_2S-H_2O	20-60	---	---	---	---	8	11
22	NH_3-CO_2-H_2O	20-60	9	7	9	10	---	---
25	NH_3-CO_2-H_2S-H_2O	20	8	12	8	12	10	11
27	NH_3-CO_2-H_2S-H_2O	20-60	---	---	---	---	8	15
	Overall Ave. Error		9	10	9	11	9	12

This comparison shows that the SWEQ model does about as well as the Van Krevelen model except that the Van Krevelen model appears to be slightly better. The overall average error from the Van Krevelen model is about 9% while the SWEQ model gives about 11%.

The picture changes considerably when high temperature data are compared as follows.

Table No.	System	Temp. Range °C	Ave. Error %					
			NH_3		CO_2		H_2S	
			VK	SWEQ	VK	SWEQ	VK	SWEQ
18	NH_3-H_2S-H_2O	80-120	45	13	---	---	33	27
19	NH_3-H_2S-H_2O	20-60	122[a]	197[a]	---	---	379[a]	265[a]
23	NH_3-CO_2-H_2O	20-199	65[a]	29[a]	105[a]	99[a]	---	---
24	NH_3-CO_2-H_2S-H_2O	50-120	108	53	84	24	146	31
	Overall Ave. Error (ignoring Tables 23 & 27)		77	36	84	24	90	29

a) Measured data in Tables 23 and 27 are believed by the author to be unreliable. Data in Table 23 deviate radically. Large and unreasonable adjustments would have to be made to correlate these data. Data in Table 27 have large deviations with little apparent pattern.

This comparison shows the SWEQ model to be superior to the Van Krevelen model at high temperatures with deviations averaging about 84% for the Van Krevelen model compared to about 29% for the SWEQ model. However, the predicition accuracy is still not as good as at lower temperatures. This can be partly explained by the fact that much higher concentrations of the components were studied in Tables 18 and 24 at high temperatures compared with concentrations in Tables 20, 22, 25, and 27 at low temperatures. Concentrations up to 14 moles/Kg of solution are covered in Tables 18 and 24 while concentrations to only about 3.5 moles/Kg of solution are covered in Tables 20, 22, 25, and 27. These higher concentrations place very high demands on the SWEQ model and makes actual correlation of the data more difficult. Besides this problem there is the normal scatter expected from the data due to measurement errors. It is not possible at this point to say which errors are correlation erros and which errors are measurement errors; however, it is possible to conclude that the sum of both errors is on the order of about 29% for the SWEQ model compared to 84% for the Van Krevelen model.

Another test for accuracy of the SWEQ model can be made by comparing mean deviations in p_{meas}/p_{calc} where the mean value is calculated as follows.

$$\left(\frac{p_{meas}}{p_{calc}}\right)_{mean\ value} = \left[\prod_{i=1,N} \left(\frac{p_{meas}}{p_{calc}}\right)_i\right]^{1/N} \qquad (43)$$

where N = number of points averaged

This comparison will show any bias errors that may exist between calculated and measured data. As in the case of average errors, the bias errors can result from either correlation bias or from bias in the experimental data. These comparisons for the SWEQ model are given in Figures 6, 7, and 8 for

NH_3, CO_2, and H_2S respectively. Figure 6 shows that mean ratios of p_{meas}/p_{calc} for NH_3 lie primarily above unity with only the data of Badger and Silver[3] and of Breitenbach and Perman lying below unity. The amount of steam required in a sour water stripper is primarily determined by the volatility of NH_3. For this reason, available NH_3 volatility data from the literature from various authors are compared in Figure 6 in an attempt to obtain a reliable volatility correlation. The author suspects that the points below unity are in error and that the true NH_3 partial pressures are slightly above unity. The scatter between various authors primarily represents bias in their measured data, but a line of unity which falls below all of these points probably represents correlation bias. This correlation bias in the case of ammonia can be easily adjusted so that measured data will scatter symmetrically both above and below unity; however, the author is hesitant to do this without further justification from other data.

Figure 7 shows that mean ratios of p_{meas}/p_{calc} for H_2S appear to fall nearly symmetrically both above and below unity, so again, the scatter between the points probably represents bias in measured data between the various authors.

Figure 9, 10, and 11 show similar plots comparing mean ratios of p_{meas}/p_{calc} from the Van Krevelen model for NH_3, CO_2, and H_2S respectively. These plots show wider scatter than it obtained from the SWEQ model. The difference has to be due to correlation bias. This result would tend to infer that there could still be correlation bias in the SWEQ model which has not been identified. If such bias exists, it has to be on the order of the deviations appearing in Figures 6 to 8 or less.

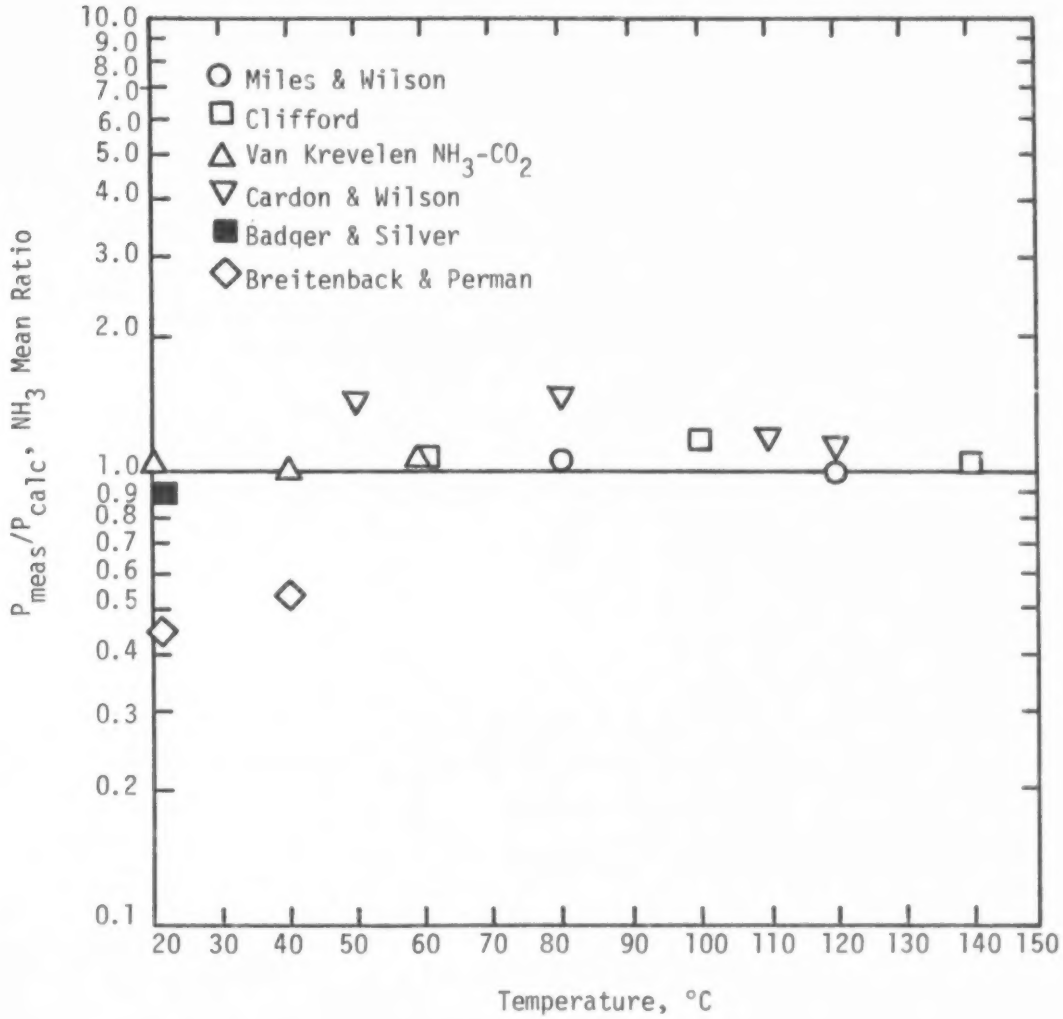

Figure 6. Ammonia mean ratio of measured over calculated partial pressures based on SWEQ correlation.

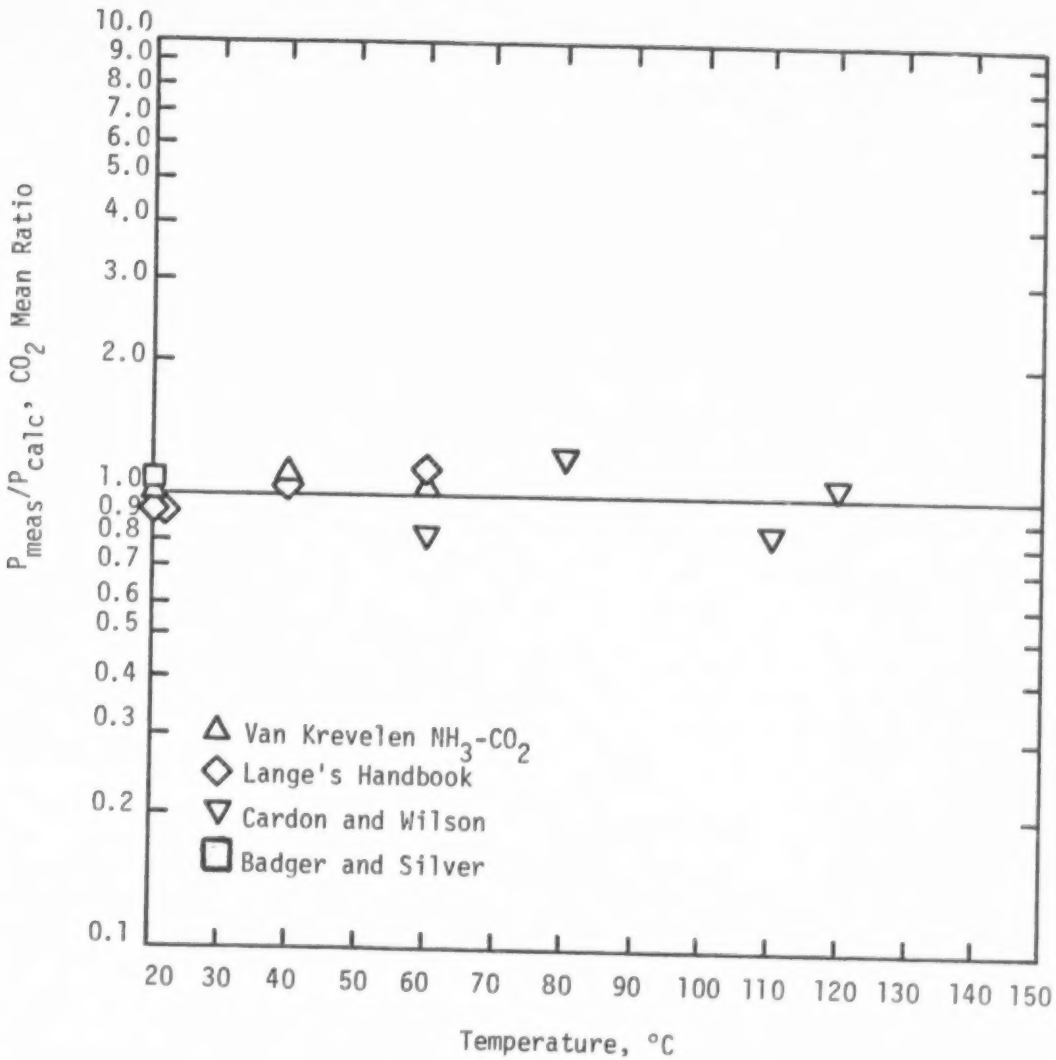

Figure 7. Carbon dioxide mean ratio of measured over calculated partial pressures based on SWEQ correlation.

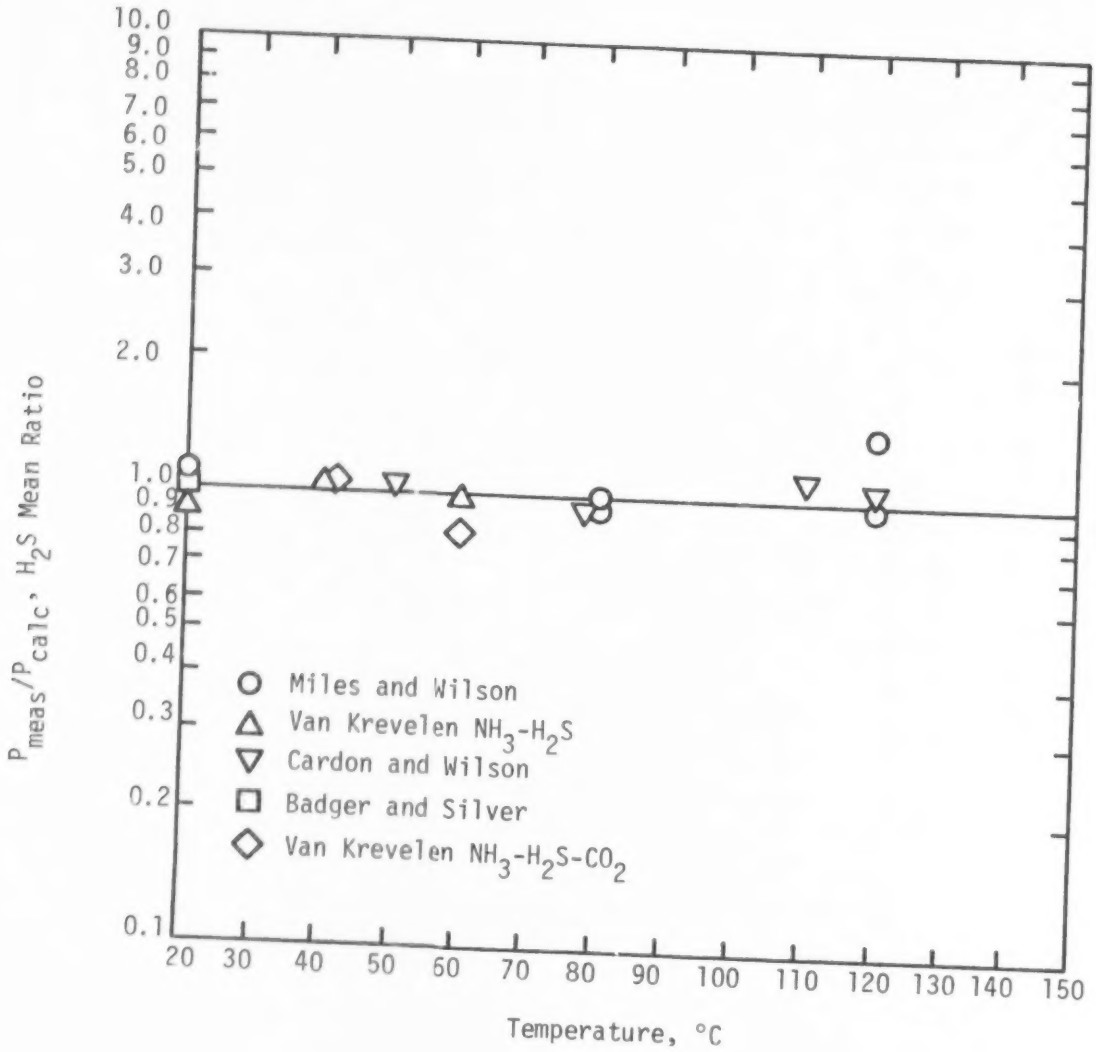

Figure 8. Hydrogen sulfide mean ratio of measured over calculated partial pressure based on SWEQ correlation.

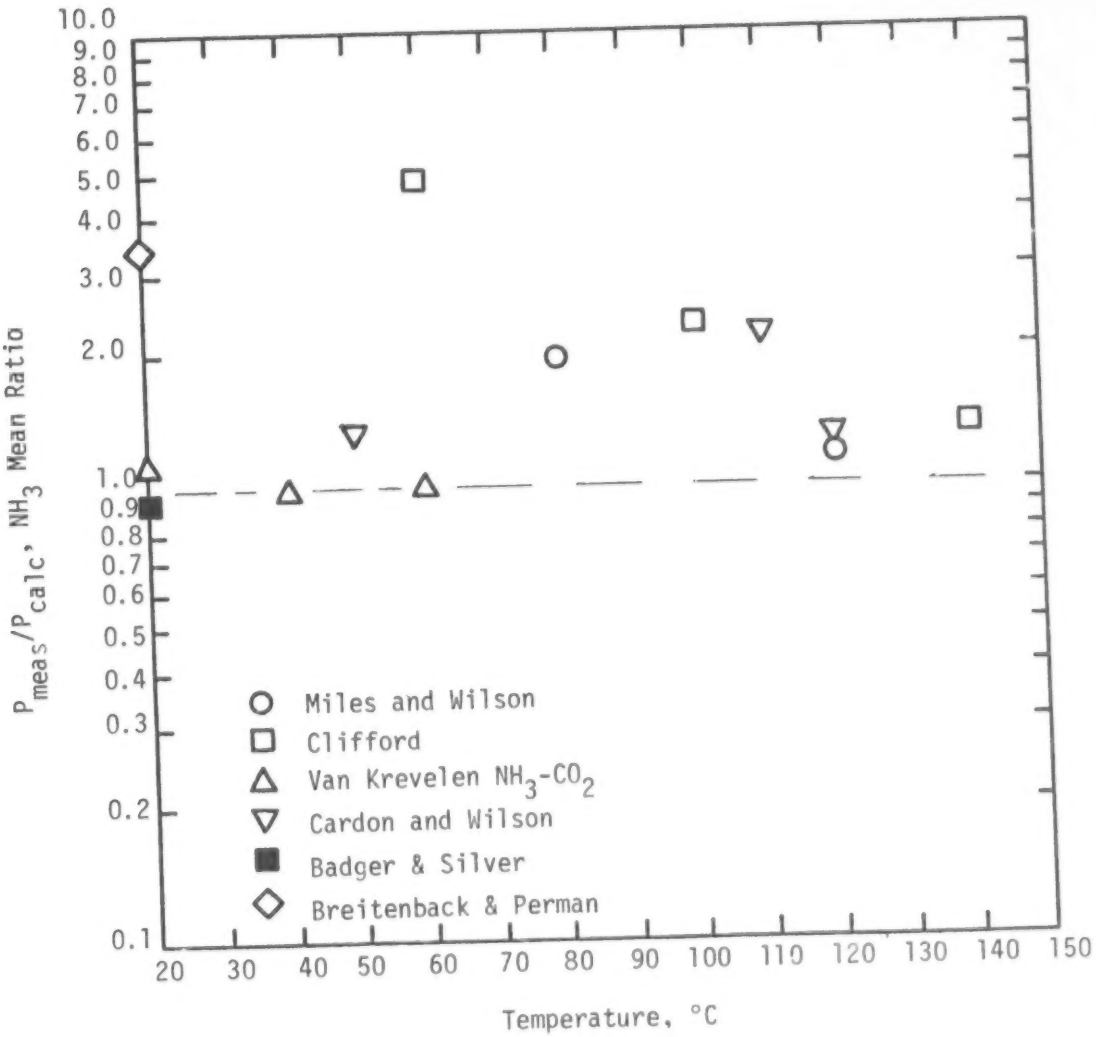

Figure 9. Ammonia mean ratio of measured over calculated partial pressures based on Van Krevelen correlation.

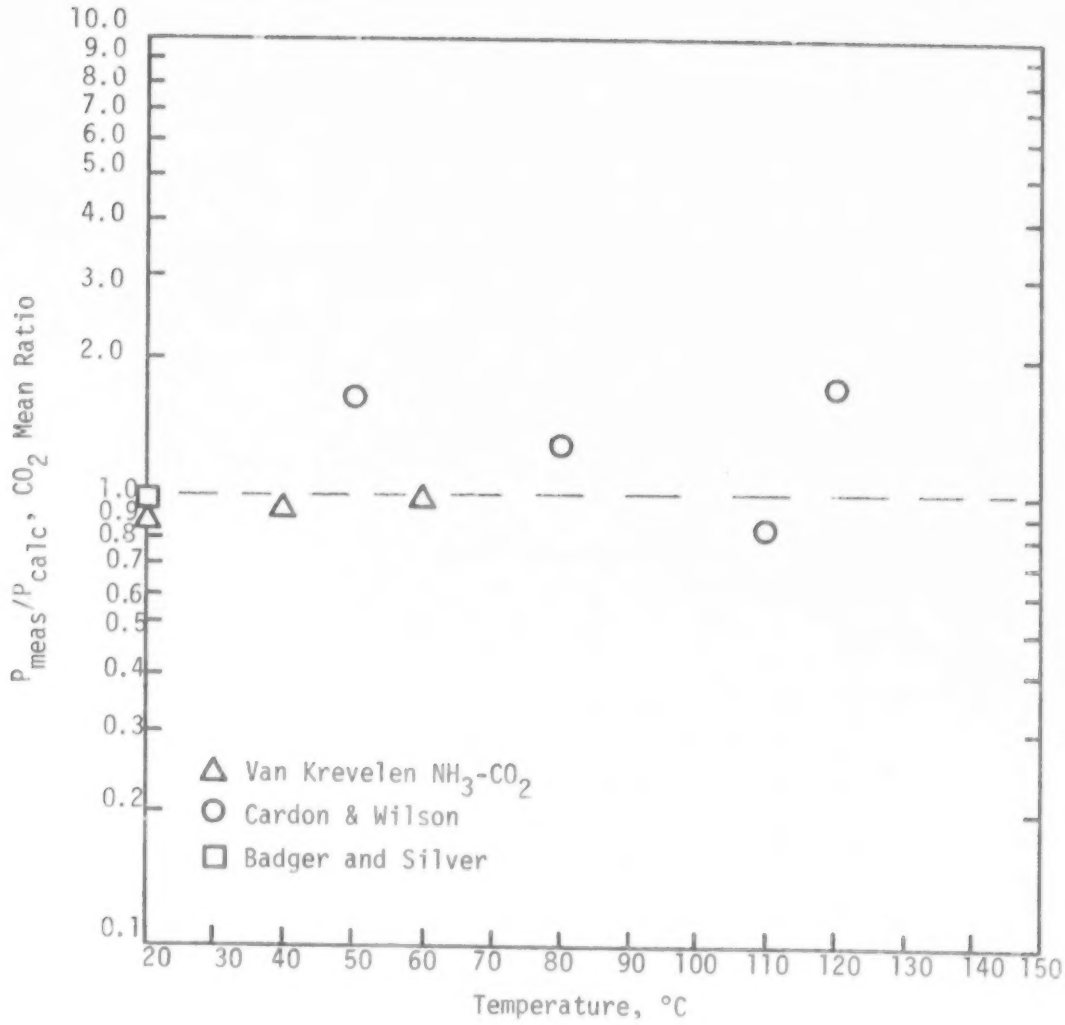

Figure 10. Carbon dioxide mean ratio of measured over calculated partial pressures based on Van Krevelen correlation.

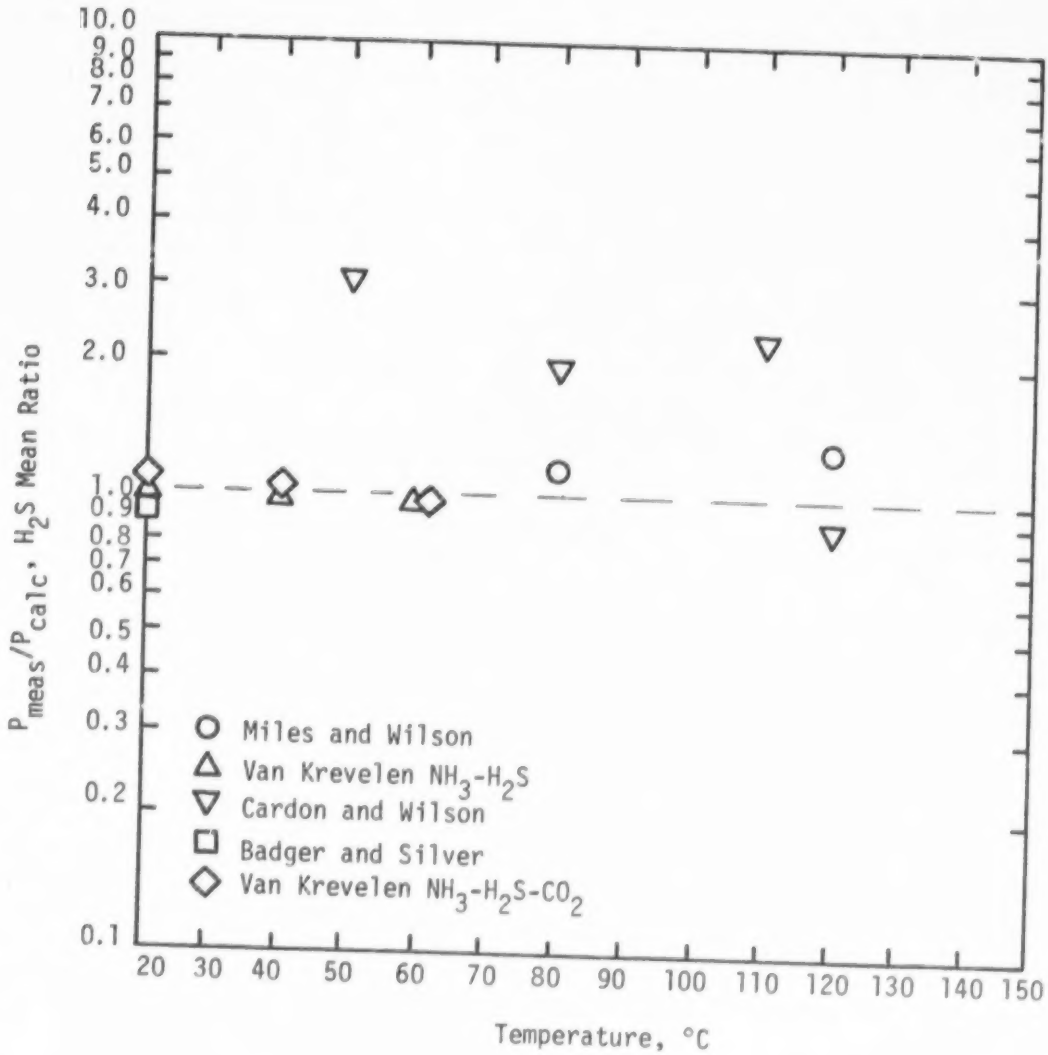

Figure 11. Hydrogen sulfide mean ratio of measured over calculated partial pressures based on Van Krevelen correlation.

Evaluation of New BYU Data

An evaluation of new NH_3-H_2S-H_2O and NH_3-CO_2-H_2S-H_2O data measured at Brigham Young University can probably be best made by comparison of measured data with predicted data from the SWEQ model. These comparisons are made in Table 18 for the H_2S-H_2O and NH_3-H_2S-H_2O systems and in Table 24 for the NH_3-CO_2-H_2S-H_2O system. The SWEQ model predicts low temperature data on which the Van Krevelen model is based with about the same accuracy as the Van Krevelen model, and at the higher temperatures from 50°C to 120°C in Tables 18 and 24, the accuracy is much better than the Van Krevelen model. As discussed above, it is not possible to separate correlation errors from measurement errors; so margins of error have to include both effects. The following gives a summary of the average errors between predicted and measured data.

Table No.	Temp. °C	No. of Points	Ave. Error % NH_3	CO_2	H_2S
18	80	10	14	--	13
	120	8	17	--	44
19	50	3	43	23	13
	80	10	77	29	47
	110	5	35	20	23
	120	5	30	25	18
Overall Ave. Error %			36	24	29

It is concluded from this comparison that the new BYU data in Tables 18 and 24 are consistent with literature data correlated by Van Krevelen et al., with average scatter between measured and correlated data being on the order of 36%, 24%, and 29% respectively for NH_3, CO_2, and H_2S. Two experimental runs given in Table 24 were ignored in computing these averages and ammonia analyses on two additional runs were ignored. The points ignored are noted at the bottom of Table 24. The reason for ignoring these points is that the deviations are so large that the experimental points appear to be unreasonable and probably in serious error.

Mean ratios of p_{meas}/p_{calc} plotted in Figures 6, 7, and 8 for NH_3, CO_2, and H_2S respectively show some bias between data in Tables 18 and 24 as follows.

Table No.	Comments
18	NH_3 appears okay H_2S appears okay
24	NH_3 at 50°C and 80°C appears about 40% too high CO_2 appears okay H_2S appears okay

Based on this comparison, it is concluded that any bias in the measured data is small except for NH_3 at 50°C and 80°C in Table 24. If these data points were ignored in computing the average error above for NH_3, then the overall average error would be reduced from 36% to 24% which is comparable to deviation erros for CO_2 and H_2S based on the SWEQ model.

Ammonia Fixation by Acids and Release by Caustic Addition

Little direct data appear in the literature on the volatilities of NH_3, CO_2, and H_2S from aqueous solutions as a function of pH. One study made by Shih et al.,[26] is given in Table 21 for the volatility of H_2S from buffered solutions. In this table, the predicted H_2S pressures are consistently lower than measured values by a factor of about 0.7. This prediction error could be the result of the salt concentration in the buffer solution which is not accounted for by the SWEQ model.

In addition to the data by Shih et al., new measurements of pH versus caustic addition have been made at BYU. These results are shown as the plotted curves in Figures 12 and 13. These comparisons show that predicted free NH_3 concentrations are also lower than measured values as occurs in the case of H_2S. These data tend to indicate that the SWEQ model might be predicting both too low H_2S and too low NH_3 partial pressures, but we doubt this based on the measured volatility data of NH_3 and H_2S examined in this report. With these discrepancies, calculated pH levels could be in error by $\pm$ 0.5 unit; this is a rather large error so more work should be done to resolve this question.

Ammonia fixation effects due to carboxylic acids and the release of NH_3 by caustic addition are predicted by the SWEQ model as given in Table 32. This table gives a comparison of calculated tray to tray NH_3, CO_2, and H_2S volatilities going down a separation column at total reflux at 20 psia column pressure. The initial vapor phase concentrations of NH_3, CO_2, and H_2S were 100 ppm on a weight basis for each component. The first set gives calculated vapor and liquid compositions for three trays under conditions of no carboyxlic acid or caustic present. In this example, the liquid concentration of all three components drops to 0.1 ppm or less on the third tray. When 500 ppm by weight or carboxylic acid is added to the liquid on each tray, then the ammonia concentration goes up to 142.4 ppm on the third tray indicating that the ammonia is fixed and is unstrippable. If caustic is then added to a level of 172.5 ppm in the liquid on each tray, then the ammonia is released from the carboxylic acid and concentrations less than 0.1 ppm are predicted for NH_3, CO_2, or H_2S in the liquid of the third tray. If too much caustic is added, then H_2S will be fixed in the liquid phase; thus 500 ppm of caustic produces an H_2S concentration in the liquid phase of the third tray of 310.1 ppm H_2S. From this table, it appears that the optimum pH for equal volatility of NH_3 and H_2S is about 8.5. This pH corresponds to the hydrogen ion concentration in the liquid phase at the temperature of the tray in the separation column. In actual practice, samples of liquid would probably be taken for pH determination at room temperature. The effect of temperature on pH can be calculated from the SWEQ model. Figure 14 gives a plot of pH at 25°C and at 120°C for the addition of caustic to the mixture shown in Figure 1. The effect of temperature will be different depending on the mixture, but this plot can give some idea of the effect.

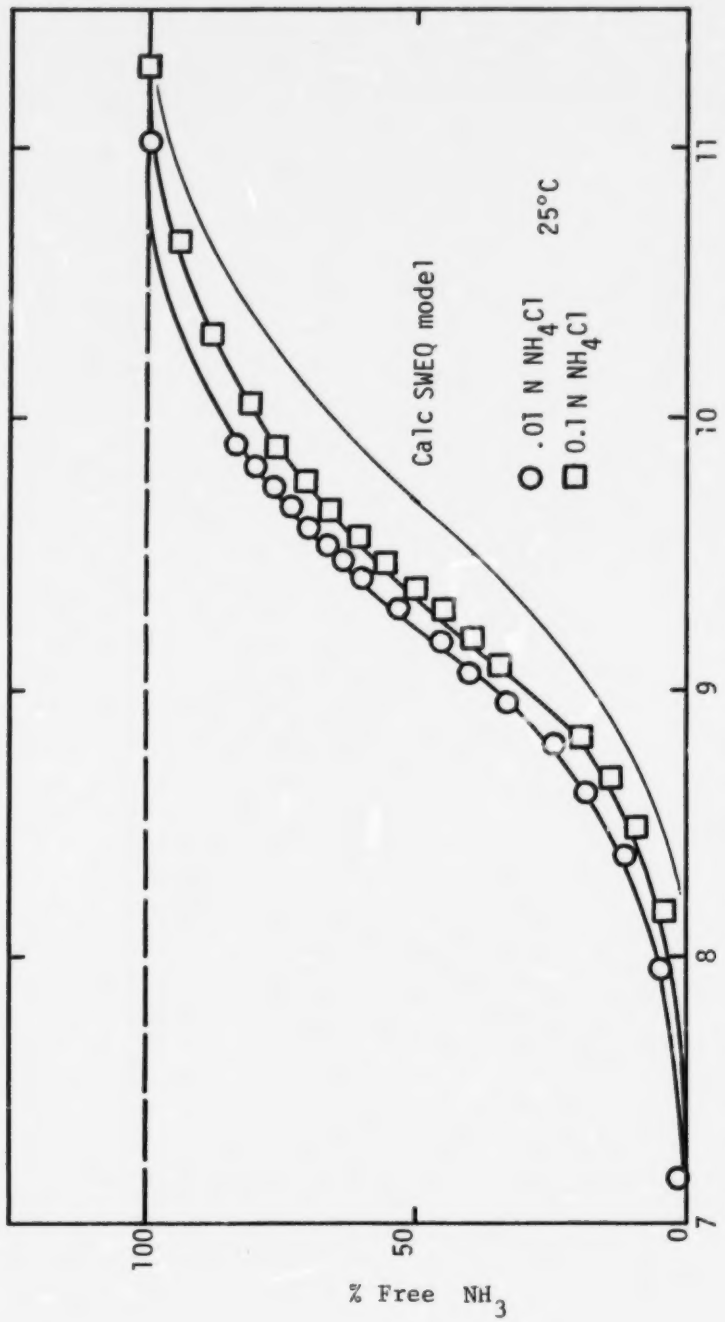

Figure 12. Free ammonia versus pH adjustment by caustic addition at 25°C.

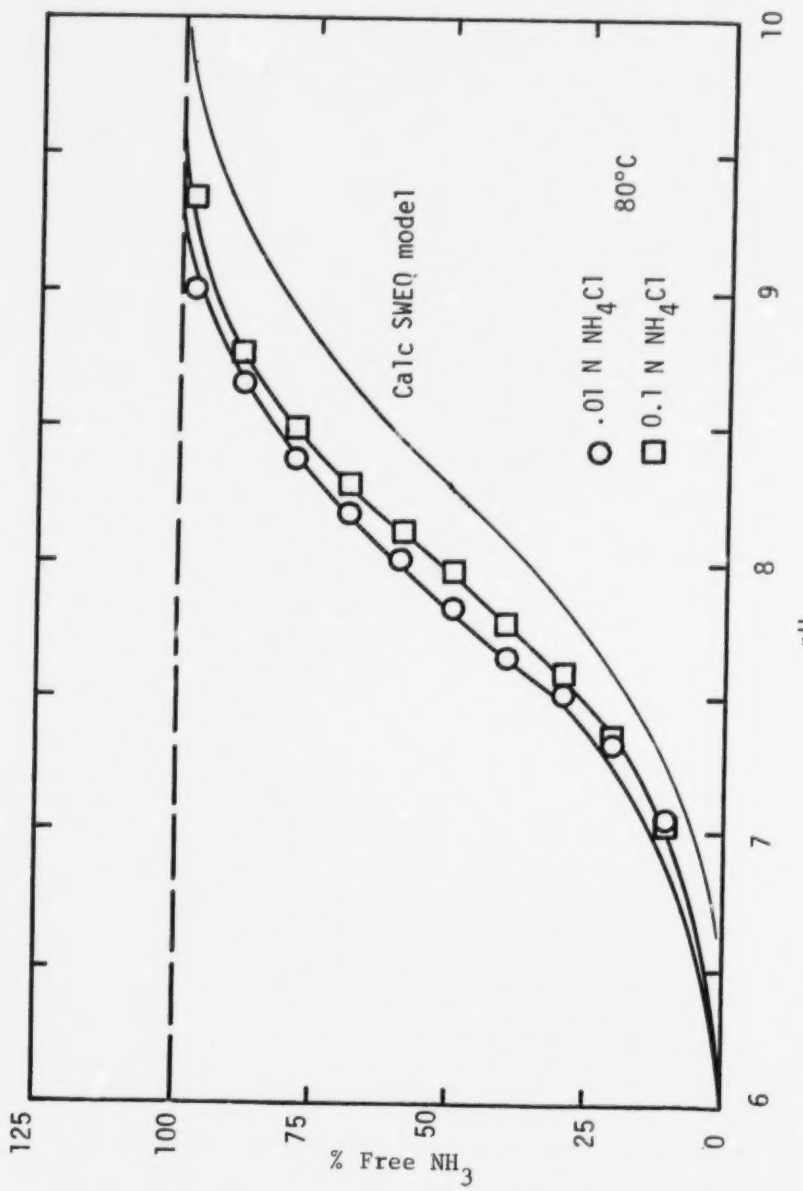

Figure 13. Free ammonia versus pH adjustment by caustic addition at 80°C.

TABLE 32. COMPARISON OF CALCULATED NH_3, CO_2, and H_2S VOLATILITES VERSUS EFFECTS FROM CARBOXYLIC ACID AND CAUSTIC ADDITION, TRAY TO TRAY FROM THE COLUMN AT TOTAL REFLUX AND 20 PSIA COLUMN PRESSURE

Tray	RCOOH or OH^- in Liquid ppm wt		Initial Basis for Each Set is 100 ppm of NH_3, CO_2, & H_2S in Vapor						Vapor/Liquid Ratio wt Basis			pH at col. Temp. in Liquid
			ppm by wt. in Vapor			ppm by wt. in Liquid						
	RCOOH	OH^-	NH_3	CO_2	H_2S	NH_3	CO_2	H_2S	NH_3	CO_2	H_2S	
1	0	0	100	100	100	5.8	3.0	1.3	17	370	78	8.035
2	0	0	5.8	0.3	1.3	0.6	0.0	0.0	9.7	1100	241	7.515
3	0	0	0.6	0.0	0.0	0.1	0.0	0.0	4.2	2590	620	7.026
1	500	0	100	100	100	138.8	0.0	0.1	.72	5600	1750	6.195
2	500	0	138.8	0.0	0.1	142.2	0.0	0.0	.98	5100	1570	6.332
3	500	0	142.2	0.0	0.0	142.4	0.0	0.0	1.00	5090	1550	6.341
1	500	172.5*	100	100	100	4.5	0.9	3.7	22*	116	27*	8.500
2	500	172.5	4.5	0.9	3.7	0.2	0.0	0.2	23	83	20	8.646
3	500	172.5	0.2	0.0	0.2	0.0	0.0	0.0	23	82	19	8.652
1	500	500	100	100	100	3.9	60.0	171.2	26	1.7	0.6	10.165
2	500	500	3.9	60.0	171.2	0.2	29.5	250.0	26	2.0	0.7	10.097
3	500	500	0.2	29.5	250.0	0.0	11.8	310.1	26	2.5	0.8	10.026

*Appears close to optimum caustic addition for best NH_3 and H_2S volatility.

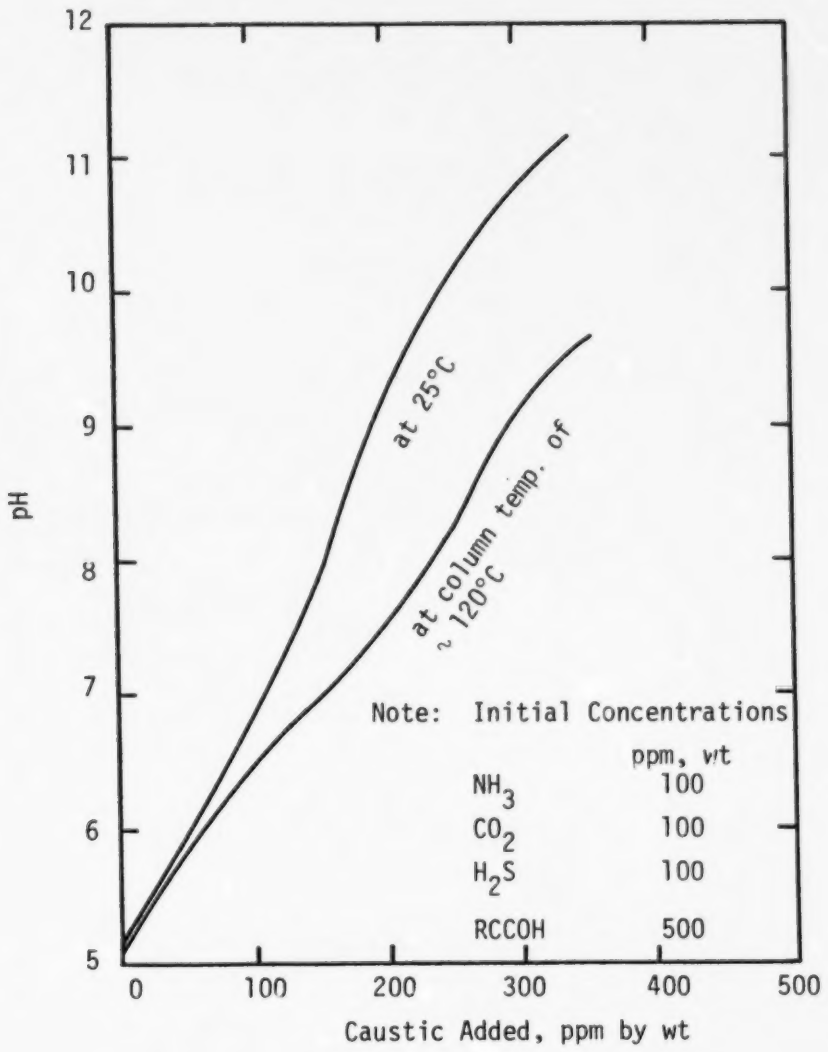

Figure 14. Sample plot of pH versus caustic addition showing variation of pH at 25°C and at column temperature.

SECTION 7

ACCURACY OF CORRELATION

The overall accuracy of the SWEQ model can be assessed by examination of the error summaries in Tables 29 to 31 for NH_3, CO_2, and H_2S respectively. From these tables, the overall average error between measured and predicted partial pressures can be summarized as follows.

Compound	Temperature Range, °C	Overall Ave. Error % VK	SWEQ
Ammonia	20 to 140°C	72	24
Carbon dioxide	20 to 120°C	35	17
Hydrogen sulfide	20 to 185°C	24	18

This comparison shows that SWEQ module is superior to the Van Krevelen model.[a)]

Data at low temperatures are represented better by both models than data at high temperatures as shown in the following comparison taken from the previous section of this report.

Compound	Ave. Error % up to 60°C VK	SWEQ	above 60°C VK	SWEQ
Ammonia	9	10	77	36
Carbon dioxide	9	11	84	24
Hydrogen sulfide	9	12	90	29

This comparison shows that both models predict the low temperature data quite well; but at high temperature, the Van Krevelen model deviates considerably from measured data, and errors between the SWEQ model and measured data increase from about 11% to about 24%.

Users of theSWEQ model must be aware that the errors summarized above are average errors and that there might be regions where the correlation is less accurate. More experimental data is required before a better assessement can be made.

[a)] This is the model published by Van Krevelen without any modifications.

SECTION 8

SUMMARY

A new correlation model has been developed for calculating sour water equilibrium data at temperatures from 20°C to 140°C. The correlating equations in this new SWEQ have been used to obtain a computer program capable of handling the various chemical and physical equilibria of NH_3, CO_2, and H_2S in sour water systems including the effects of carboxylic acids on NH_3 fixation and release by caustic addition.

This new SWEQ correlation model has been used to evaluate published and new vapor-liquid equilibrium data and comparisons are made with the Van Krevelen prediction equations as published by Van Krevelen. Average errors between calculated and measured partial pressure data can be summarized as follows.

	Ave. Error %			
	up to 60°C		above 60°C	
Compound	VK	SWEQ	VK	SWEQ
Ammonia	9	10	77	36
Carbon dioxide	9	11	84	24
Hydrogen sulfide	9	12	90	29

This comparison shows that both models predict low temperature data quite well; but at high temperatures, the Van Krevelen model deviates considerably from measured data, and errors between the SWEQ model and measured data increase from about 11% to about 29%. Comparisons with variations of the Van Krevelen model as published by other authors have not been made.

Vapor-liquid equilibrium measurements made at Brigham Young University are predicted by the SWEQ model with the following average errors.

Compound	Ave. Error %
Ammonia	36
Carbon dioxide	24
Hydrogen sulfide	29

Data on measured NH_3 partial pressures from NH_3-CO_2-H_2S-H_2O mixtures appear too high by about 40% at 50°C and 80°C. If these points are ignored, then the average ammonia error is reduced from 36% to 24%.

Details of the SWEQ correlation model, correlating equations, the computer program, and evaluations of experimental data are given in this report.

REFERENCES

1. D. W. Van Krevelen, P. J. Hoftijzer, and F. J. Huntjens, Recueil Des Travaux Chimiques Des Pays-Bas, 68, 191-216 (1949).

2. M. R. Beychok, Aqueous Wastes from Petroleum and Petrochemical Plants, John Wiley & Sons, New York, N.Y., (1967).

3. T. J. Edwards, J. Newman, and J. M. Prausnitz, AIChE Journal, 21, 248 (1975).

4. R. L. Kent and B. Eisenberg, Hydrocarbon Processing, Feb., 87-90 (1976).

5. D. L. Cardon and G. M. Wilson, "Ammonia-Carbon Dioxide-Hydrogen Sulfide-Water Vapor-Liquid Study", Final Project Report in progress for the API.

6. D. C. Bomberger and J. H. Smith, Report on "Evaluation of Ammonia 'Fixation' Components in Actual Refinery Sour Waters", Stanford Research Institute, December 10, 1977.

7. H. S. Harned and S. R. Scholes, J. of Amer. Chem. Soc., 63, 1706 (1941).

8. Cuta and Stratfelda, Chem. Listy, 48, 1308 (1954).

9. B. N. Ryzhenko, Geokhemiya, 137-138 (1963).

10. Handbook of Chemistry and Physics, 51st ed., The Chemical Rubber Co., D-122.

11. Handbook of Physical Constants, Revised ed., The Geological Society of America, Memoir 97, Sec. 18 (1966).

12. A. L. Ellis and N. B. Milestone, Geochim. Cosmochim. Acta, 31, 615 (1967).

13. Handbook of Chemistry and Physics, 51st ed., The Chemical Rubber Co., D-143-D-144 (1970-71).

14. American Petroleum Institute, Publication No. 946, "Sour Water Stripping Project Committee on Refinery Environmental Control, American Petroleum Institute", June 1975.

15. E. H. M. Badger and L. Silver, J. Soc. Chem. Ind., 57, 110-12 (1938).

16. Breitenbach, Bull. Univ. Wis. Eng. Exp. Sta. Ser. 68 (as given in Perry's Chemical Engineers' Handbook, Fouth ed., 1963).

17. I. L. Clifford and E. Hunter, J. Phys. Chem., 37, 101 (1933).

18. I. G. C. Dryden, J. Soc. Chem. Ind., 66, 59 (1947).

19. S. Ikenko, Kogyo Kagaku Zasshi, 64, 627 (1961).

20. Lange's Handbook of Chemistry, Eighth ed., 1952 (original source not given).

21. D. H. Miles and G. M. Wilson, "Vapor-Liquid Equilibrium Data for Design of Sour Water Strippers", Annual Report to API for 1974, October 1975.

22. E. Otsaka, S. Yoshimura, M. Yokabe, S. Inque, Kogyo Kagaku Zasshi, 63, 1214-1218 (1960).

23. E. P. Perman, J. Chem. Soc. London, 83, 1168 (1903).

24. Sherwood, Inq. Eng. Chem., 17, 745 (1925). (as given in Perry's Chemical Engineers' Handbook, Fouth ed., 1963).

25. S. Pexton and E. H. M. Badger, J. Soc. Chem. Ind., 57, 106 (1938).

26. T. T. C. Shih, B. F. Hrutfiord, K. V. Sarkanen, and L. N. Johansen, TAPPI, Technical Assoc. of the Pulp and Paper Industry, 50, (No. 12) 630-634 (1967).

27. T. Takahashi, Kogyo Kagaku Zasshi, 65, 837-843 (1962).

28. T. Takahashi, S. Yoshimura, K. Fukii, and E. Otsaka, Kogyo Kagaku Zasshi, 65, 743-745 (1962).

29. V. E. Terres, W. Attiq, and F. Tscherter, Gas. u. Wasserfach, 98, 512-516 (1957).

30. M. E. Jones, J. Phys. Chem. 67, 1113-1115 (1963).

31. S. D. Malinin, Geochem. Int., 11, 1060-75 (1975).

32. T. N. Kozintseva, Geochem. Int., No. 4, 750-756 (1964).

33. V. I. Oratovskii, A. M. Gamolskii, and N. N. Klimenko, J. Appl. Chem. USSR, 37, 2363-2367 (1964).

34. H. Gamsjager and P. Schindler, Helv. Chim. Acta, 52, 1395-1402 (1969).

35. T. N. Kozintseva, Geokhemiya, 121-134 (1965).

36. J. L. Vogel, M.S. Thesis, The University of Tulsa, 1971.

37. G. J. Frohlich, Ph.D. Thesis, Polytechnic Institute of Brooklyn University, Microfilms No. 60-3497, 1957.

38. M. R. Beychok, Hydrocarbon Processing, Sept., 261-263 (1976).

APPENDIX

COMPUTER PROGRAM FOR CALCULATING SOUR WATER EQUILIBRIA BASED ON THE VAN KREVELEN EQUATIONS

Table 33 gives a listing of the computer program used for calculating NH_3, CO_2, H_2S and H_2O partial pressure data for comparing the SWEQ model with the Van Krevelen [1,2] equations. The input and output of this program is very similar to the SWEQ model.

The main calculations are done starting with the following statement.

```
DO 2030 I = 1,100
```

This is the start of an iteration loop which extends to statement 2030. This iteration loop calculates the amount of $CO_3^=$ (BT) and H_2NCOO^- (EPS) in solution for various assumed concentrations of HCO_3^- (AE). The concentration of HCO_3^- is adjusted in each iteration so that the total of HCO_3^- + $CO_3^=$ + H_2NCOO^- concentrations add to the CO_2 content of the mixture. The following Fortran symbols are used for the chemical equilibrium constants.

EK1	$CO_{2(g)} + NH_3 + H_2O \rightarrow NH_4^+ + HCO_3^-$	(A-1)
EK2	$NH_4^+ + HCO_3^- \rightarrow H_2NCOO^- + H_2O$	(A-2)
EK3	$NH_3 + HCO_3^- \rightarrow NH_4^+ + CO_3^=$	(A-3)
EK4	$H_2S_{(g)} + NH_3 \rightarrow HS^- + NH_4^+$	(A-4)

Other symbols have the same meaning as symbols in the SWEQ computer program. After correct values of HCO_3^-, $CO_3^=$, and H_2NCOO^- concentrations are found, the program proceeds to calculate NH_3, CO_2, H_2S and H_2O partial pressures and vapor concentrations. The results are then printed out.

This Van Krevelen computer program only computes vapor composition and pressure from a specified liquid composition and temperature. No other options were programmed. The equations for the chemical equilibrium constants and ammonia Henry's constant were obtained by fitting tabular values given by Van Krevelen. The Henry's constant of ammonia above 90°C is based on Beychok's [2] graphical extrapolation. Because of the tabular and graphical nature of Van Krevelen's correlation and the graphical nature of the Henry's constant for ammonia given by Beychok, there is some arbitrariness in the computer program because another person using different equations to fit the tabular data and graphs would obtain slightly different results.

Beychok no longer recommends the ammonia Henry's constant published in his book,[38] but comparison is made with the book because it represents a basis for comparing any changes or variations.

Further discussion of the Van Krevelen correlation can be obtained by referring to either Beychok[2] or Van Krevelen.[1]

TABLE A-1. COMPUTER PROGRAM USED FOR CALCULATING VAPOR-LIQUID EQUILIBRIUM DATA FROM THE VAN KREVELEN CORRELATION

```
      OPEN(UNIT=20,DEVICE='DSK',ACCESS='SEQIN',FILE='SW30')
      DATA WA,WC,WS,WW/17,03,44,01,34,08,18,02/
      RHO = 1
2     READ(20,1000) TC,XA,XC,XS,XW
      TK = TC+273,15
      TR = TK*1,8
      XA = XA+1E-19
      XC = XC+1E-19
      XS = XS+1E-19
      XW = XW+1E-19
250   F = 1000*RHO/(XA+XC+XS+XW)
      CA = XA*F/WA
      CC = XC*F/WC
      CS = XS*F/WS
      AL = CC
      EK2 = EXP(-5,37+1925/TK)
      EK3 = EXP(-18,19+4752/TK)
      CCS = 0
      GA = CS
      CSS = 0
      SD = 0
      DO 2030 I=1,100
      CAS = CA+AL-1.5
      IF(CAS) 1994,1994,1996
1994  PA = 0
      PC = 0
      PS = 0
      GO TO 1501
1995  FORMAT(' H2S AND CO2 IN EXCESS')
      GO TO 1501
1996  EPS = EK2*CAS*AL
      DE = CA-CAS-EPS
      IF(DE) 2000,2000,2010
2000  BT = 0
      GO TO 2020
2010  BT = EK3*CAS*AL/DE
2020  CCE = AL+EPS+BT
      IF(ABS(ALOG(CCE/CC))-,0001) 3000,3000,2030
2030  AL = AL+(,5+,5*CC/CCE)
      WRITE(5,2040)
2040  FORMAT(' ITERATION DID NOT CONVERGE IN 100 CYCLES')
3000  HW = EXP(14,465-6996,6/(TR-77,67))
      IF(TC-90) 3020,3010,3010
3010  HAO = EXP(-3,17-,022*TC)
      GO TO 3030
3020  HAO = EXP(-17,03+4315/TK)
3030  HA = ,92*HAO*EXP(,0576*CAS)
      HA = 1/(HA+51,71)
      PA = 51,71*HA*CAS
      TNW = (1000*RHO-CA*WA-CC*WC-CS*WS)/WW-AL+EPS
      TNM = CA+CC+BT-DE+GA+SD+TNW+CS
      PW = HW*TNW/TNM
```

This is a test to see if the ratio of NH_3/acid gas is greater than 1.5 If not so, then the computation is skipped.

Iteration loop to calculate amounts of HCO_3^-, $CO_3^=$, and H_2NCOO^-

(continued)

Reproduced from best available copy.

TABLE A-1. (continued)

```
      ELI = (AL+4*BT+DE+EPS+CS)/2
      EK1 = .97*EXP(-25.42+6535/TK+(-1.32+866/TK)*ELI**.4)
      EK4 = -EXP(-1.784+.627*ALOG(TC))+.089*CS*(1.929-539/TK)*CC
      EK4 = EXP(2.30259*EK4)
      PC = 51.71*DE*AL/(EK1*CAS*51.71)
      PS = 51.71*DE*CS/(EK4*CAS*51.71)
      P = PA+PC+PS+PW
      YA = PA/P
      YC = PC/P
      YS = PS/P
      YW = PW/P
1501  XA = 100*CA*WA/(1000*RHO)
      XC = 100*CC*WC/(1000*RHO)
      XS = 100*CS*WS/(1000*RHO)
      XW = 100-XA-XC-XS
      YT = YA*WA+YC*WC+YS*WS+YW*WW
      YA = 100*YA*WA/YT
      YC = 100*YC*WC/YT
      YS = 100*YS*WS/YT
      YW = 100*YW*WW/YT
      WRITE(5,1030) TC,P,PH
      WRITE(5,1020)
      EK = YA/XA
      WRITE(5,1040) XA,YA,EK
      EK = YC/XC
      WRITE(5,1050) XC,YC,EK
      EK = YS/XS
      WRITE(5,1060) XS,YS,EK
      EK = YW/XW
      WRITE(5,1070) XW,YW,EK
      GO TO 2
1000  FORMAT(10E)
1001  FORMAT(2I)
1010  FORMAT(' PH DID NOT CONVERGE IN 100 CYCLES')
1011  FORMAT(' TEMPERATURE DID NOT CONVERGE IN 100 CYCLES')
1020  FORMAT(' COMPONENT          LIQUID     VAPOR    K-VALUE')
1030  FORMAT(//' TEMPERATURE, C',F8.2,/' PRESSURE, PSIA',F8.2,/
     112X' PH',F8.2,I6//)
1040  FORMAT(' AMMONIA           ',3F10.5)
1050  FORMAT(' CARBON DIOXIDE    ',3F10.5)
1060  FORMAT(' HYDROGEN SULFIDE',3F10.5)
1070  FORMAT(' WATER             ',3F10.5)
1080  FORMAT(X,F4.0,3F7.3,7F6.2,9F6.3,F6.2)
      END
```